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Radian Corp., Austin, TX

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EVALUATION OF VOC EMISSIONS FROM WASTEWATER SYSTEMS (SECONDARY EMISSIONS)

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Cincinnati, Ohio 45268

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The technical objective of this project was to obtain data for evaluating volatile carbon (VOC) emissions from wastewater treatment facilities for the synthetic organic chemicals manufacturing industry (SOCMI). VOC emissions data were obtained using the Concentration-Profile technique and were compared to emission rate data obtained by predictive modeling. Methods for sampling and analysis of VOC emissions in ambient air were evaluated and refined to obtain the necessary data. The comparison of measured and predicted flux rates was performed on data obtained from two wastewater treatment facilities; one that used forced aeration and one anaerobic facility.

The field sampling procedure (Concentration-Profile) involved determining temperature, wind speed and VOC species concentrations at six logarithmically spaced heights above the water surface. VOC species were determined by collecting time integrated air samples in evacuated stainless steel canisters and analyzing these by cryogenic concentration and high resolution gas chromatography using simultaneous flame ionization and photoionization detection.

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FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from organic chemical plant wastewater treatment systems. The study was conducted to provide a better understanding of the quantity and characteristics of air emissions from wastewater treatment systems. Further information on this subject may be obtained from the Organic and Inorganic Chemicals and Products Branch, Industrial Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act and solid waste legislation. If control technology is unavailable, inadequate or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

IERL has the responsibility for developing control technology for a large number of operations (more than 500) in the chemical and related industries. As in any technical program, the first step is to identify the unsolved problems. Each of the industries is to be examined in detail to determine if there is sufficient potential environmental risk to justify the development of control technology by IERL.

Radian Corporation was contracted with EPA to investigate the environmental impact of volatile organic compound (VOC) emissions from wastewater treatment systems at synthetic organic chemical manufacturing plants. Both field sampling and analysis results and calculated emissions were developed for wastewater treatment systems.

This study was undertaken to provide information on air emissions from wastewater treatment systems. It was initiated by the Industrial Pollution Control Division of IERL-Cincinnati in March 1981. Mr. Paul de Percin of the Organic and Inorganic Chemicals and Products Branch served as EPA Project Leader to the project.

ABSTRACT

The technical objective of this project was to obtain data for evaluating volatile carbon (VOC) emissions from wastewater treatment facilities for the synthetic organic chemicals manufacturing industry (SOCMI). VOC emissions data were obtained using the Concentration-Profile technique and were compared to emission rate data obtained by predictive modeling. Methods for sampling and analysis of VOC emissions in ambient air were evaluated and refined to obtain the necessary data. The comparison of measured and predicted flux rates was performed on data obtained from two wastewater treatment facilities; one that used forced aeration and one anaerobic facility.

The field sampling procedure (Concentration-Profile) involved determining temperature, wind speed and VOC species concentrations at six logarithmically spaced heights above the water surface. VOC species were determined by collecting time integrated air samples in evacuated stainless steel canisters and analyzing these by cryogenic concentration and high resolution gas chromatography using simultaneous flame ionization and photoionization detection.

VOC emissions were measured using a modification of the C-P technique (1) at two chemical waste treatment facilities, one using an aerobic bio-oxidation pond (site FB), and the second using a non-aerated pond (site TB). Emissions from both sites were very low, near the detection limits for the sampling and analytical methods which were used (3 ppbv-C). VOC flux rates were determined for benzene, diethyl ether, indene and styrene at site FB. Also, a flux rate was determined for the total aromatic content in the air above the pond surface. Measured flux rates at this site ranged from 430 kg/Ha-yr for styrene to 3660 kg/Ha-yr for diethyl ether. The average flux rate for total aromatics at this site was 20,400 kg/Ha-yr. VOC flux rates at site TB were determined for benzene, cyclohexane and acetone. Measured flux rates at this site ranged from 130 kg/Ha-yr for benzene to 1550 kg/Ha-yr for acetone. Standard errors and confidence limits were calculated for all analytical and meteorological measurements. Because of the low levels of VOC species which were present above the ponds and sampling and analytical variabilities, a zero flux rate was within the 95% confidence level for all flux measurements.

Flux rates determined using the modified C-P technique were compared to flux rates obtained by predictive modeling. Results of the comparison were variable, and seemed to be related to the type of compound and whether or not aerators were used. The lower predicted flux rates for the polar compounds can possibly be attributed to low analytical data on these compounds in water, since these do not purge efficiently using routine purge and trap techniques. For the site containing aerators (FB), predictive flux rates for

the three aromatic compounds were approximately 3.5 times higher than measured flux rates. However, for diethyl ether, the predicted flux rate was only 35% of the measured flux rate. Predicted flux rates for diethyl ether and styrene were within the 95% confidence limits for the measured rates, while benzene and styrene were outside the 95% confidence limits. The predictive model indicated that 85-95% of the overall emissions resulted from aeration (turbulent phase).

For the site not containing aerators (TB), predictive flux rates for benzene and cyclohexane were greater than measured rates by factors of 10.0 and 5.9, respectively. The predicted flux rate for acetone at this site was 15% of the measured rate. The predicted flux rate for acetone was within the 95% confidence limits for the measured value, while predicted flux rates for benzene and cyclohexane were not.

Results of the quality assurance/quality control portion of this project indicated that the overall chemical data accuracy was -12% and the combined sampling and analytical precision (variability) for ambient species measurements was ±34%.

This report was submitted by Radian Corporation in fulfillment of Work Assignment Number SBR04 of Contract Number 68-03-3038 under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from April 1, 1981 to August 1, 1983.

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ABBREVIATIONS AND SYMBOLS

CC - cryogenic concentration

CDS - chromatography data system (Varian Vista 401 CDS)

C-P technique - the Concentration-Profile technique for measuring flux rates (1)

CV - coefficient of variation (standard deviation/mean X 100%)

DART - Data Acquisition/Reduction Terminal; computer system for field data capture

EPA - Environmental Protection Agency

FB - test site 1, aerobic treatment facility

FID - flame ionization detector

GC - gas chromatograph

GC/FID/PID - gas chromatography with simultaneous flame ionization and photoionization detection

GC/MS - gas chromatography/mass spectrometry

Ha - hectare (10,000 m^2)

NBS - National Bureau of Standards

ng-C - nanograms carbon

nL-C - nanoliters carbon

PID - photoionization detector

PID/FID ratio - the response ratio of photoionization and flame ionization detectors to a given compound

ppbv-C - parts-per-billion of carbon by volume

ppmv-C - parts-per-million of carbon by volume

PT - purge and trap

ABBREVIATIONS AND SYMBOLS (Continued)

QA - quality assurance

QAPP - Quality Assurance Project Plan

QC - quality control

r - correlation coefficient

R_i - Richardson number - used to estimate atmospheric stability

RSD - relative standard deviation

RRT - relative retention time

s.s. - stainless steel

SOCMI - synthetic organic chemicals manufacturing industry

TB - test site 2, anaerobic treatment facility

TD - thermal desorption

TNMHC - total non-methane hydrocarbon content

TPO - technical project officer

TNR - toluene normalized response as applied to simultaneous PID/FID detection

total C_2 - ethane, ethylene and acetylene

total C_3 - propane and propylene

UHP - ultra high purity grade of a given gas

V - pooled variance

VOC - volatile organic compound

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The authors would like to acknowledge and thank the following individuals for their contributions to this project. Special thanks are extended to Mr. Paul de Percin of the U.S. EPA Organic and Inorganic Chemical Products Branch, IERL, Cincinnati, Ohio, who served as the Technical Project Officer, and Mr. William Lonneman of the U.S. EPA Gas Kinetics and Photochemistry Branch, ESRL, Research Triangle Park, North Carolina, for lending the necessary sample containers. The authors would also like to acknowledge Dr. Roger Minear of the Department of Civil Engineering, the University of Tennessee, who was the original technical lead on the project.

SECTION 1

INTRODUCTION

The technical objective of this study was to examine and refine a method for the sampling of volatile organic carbon (VOC) emissions from wastewater treatment facilities for the synthetic organic chemicals manufacturing industry (SOCMI), and to evaluate a predictive model using actual emissions data. The method that was refined and used to measure VOC emissions was the Concentration-Profile (C-P) Technique developed for EPA by the University of Arkansas (1). The procedure involved field determinations of temperature, wind speed and time averaged concentrations of VOC and specific compounds, all as a function of distance above the wastewater pond surface using a logarithmic interval design. VOC species and chemical class concentrations were measured at two sites using the C-P technique. These concentrations were compared to emissions predicted using the models developed by Thibodeaux and Hwang (1,2).

Initial portions of this study were directed toward evaluation of the sampling restrictions of the C-P technique, site visits, site selection and evaluation of techniques for collecting VOC species. Results of these phases of the project can be found in previous reports (3-5). After the model requirements, sampling sites and methods of sampling had been established and approved by the EPA Technical Project Officer (TPO), the field sampling portion of this project was initiated. A site-specific test plan (6) and a quality assurance project plan (QAPP) (7) were then prepared and approved by the TPO.

In this document, results of the field sampling and analysis portion of the project are reported. Concentration-Profile sampling was performed in triplicate at each of two sites. At the first site, sampling was performed on an aerobic biological treatment pond. C-P sampling at the second site was performed on a non-aerated pond. VOC flux rates were calculated from field data and laboratory analyses of air samples using the C-P technique. The predictive model was then applied to selected VOC species, using concentrations measured in water samples collected at the sites. Measured and predicted flux rates were then compared.

All results are presented in Section 7 of this document. Conclusions and recommendations based on these results are presented in Section 2. Sampling and analytical methods are discussed in Sections 3 and 4, respectively, and experimental matrices are presented in Section 5. All data reduction and processing methods and calculations used for the flux and predictive models are discussed in Section 6. A thorough quality assurance/quality control program was designed and implemented for this study. These results are presented in Section 8.

The results of one portion of this project, the development of multisorbent sampling tubes for collecting VOC species, are not reported in this document. The results of this study are reported in a supplemental technical note (8).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations based on the experimental and predictive model results from Section 7 and the quality assurance/quality control results from Section 8 are discussed below.

VOC emissions were measured using a modification of the C-P technique (1) at two chemical waste treatment facilities, one using an aerobic bio-oxidation pond (site FB), and the second using a non-aerated pond (site TB). Emissions from both sites were very low, near the detection limits for the sampling and analytical methods which were used (3 ppbv-C). VOC flux rates were calculated for benzene, diethyl ether, indene and scyrene at site FB. Also, a flux rate was determined for the total aromatic content in the air above the pond surface. Measured flux rates at this site ranged from 430 kg/Ha-yr for styrene to 3660 kg/Ha-yr for diethyl ether. The average flux rate for total aromatics at this site was 20,400 kg/Ha-yr. VOC flux rates at site TB were determined for benzene, cyclohexane and acetone. Measured flux rates at this site ranged from 130 kg/Ha-yr for benzene to 1550 kg/Ha-yr for acetone. Standard errors and confidence limits were calculated for all analytical and meteorological measurements. Because of the low levels of VOC species which were present above the ponds and sampling and analytical variabilities, a zero flux rate was within the 95% confidence level for all flux measurements.

Flux rates determined using the modified C-P technique were compared to flux rates predicted by the models of Thibodeaux and Hwang (1,2). Results of the comparison were variable, and seemed to be related to the type of compound and whether or not aerators were used. For the site containing aerators (FB), predictive flux rates for the three aromatic compounds were approximately 3.5 times higher than measured flux rates. However, for diethyl ether, the predicted flux rate was only 35% of the measured flux rate. Predicted flux rates for diethyl ether and styrene were within the 95% confidence limits for the measured rates, while benzene and styrene were outside the 95% confidence limits. The predictive model indicated that 85-95% of the overall emissions resulted from aeration (turbulent phase).

For the site not containing aerators (TB), predictive flux rates for benzene and cyclohexane were greater than measured rates by factors of 10.0 and 5.9, respectively. The predicted flux rate for acetone at this site was 15% of the measured rate. The predicted flux rate for acetone was within the 95% confidence limits for the measured value, while predicted flux rates for benzene and cyclohexane were not.

As presented, the C-P technique called for collecting VOC species using liquid oxygen traps for field sampling. This method presented a number of safety and procedural problems and, therefore, was not used. Instead, air samples were collected in evacuated stainless steel canisters using vacuum flow regulators to obtain integrated samples. Extreme care must be used to minimize contamination with this technique. However, it is a simpler and more workable technique than using liquid oxygen traps.

Results of the quality assurance/quality control portion of this project indicated that the overall chemical data accuracy was -12% and the combined sampling and analytical precision (variability) for ambient species measurements was ±34%.

The C-P technique used to measure flux rates is an indirect measurement technique since it requires micrometeorological modeling to convert measured concentrations to flux rates. Validation of the predictive model should only be considered a relative comparison between the predictive model and the micrometeorological model used for measuring flux rates. In the future, it is recommended that both models be compared to emission rates determined by a direct measurement technique. The meteorological and height-to-berm requirements of the C-P technique seriously limit its applicability on smaller ponds. Some treatment facilities use small settling and cooling ponds prior to larger scale treatment. Because of elevated temperatures and concentrations in these ponds, they can potentially produce significant emissions. A measurement technique should be developed and evaluated for smaller ponds.

SECTION 3

SAMPLING METHODS

The determination of chemical flux rates above waste treatment ponds required measurements of wind speed, temperature and organic species concentrations at six logarithmically spaced heights over the pond surface. In addition, measurements of humidity, water temperature and organic composition of the water were required. A 20-foot pontoon boat was outfitted with the necessary equipment to provide these measurements and with safety equipment for sampling personnel. The sampling equipment consisted of a 4-meter mast with six wind speed sensors, six temperature sensors and seven air collection probes, a continuous real-time data collection system, water temperature and sampling equipment and an instrument for measuring humidity. The functions of each of these and sampling procedures are discussed in this section.

MAST DESCRIPTION

A diagram of the mast sample collection system is presented in Figure 3-1. This system consisted of a mast supporting six sensor arms, a side panel housing all meteorological measurement controls and a computer data system. Each sensor arm located on the mast was spaced in a logarithmic fashion. The mast position could be adjusted so that the bottom arm was at water level. Each sensor arm supported one temperature sensor, one cup anemometer for measuring wind velocity and one air sampling probe. The second sensor arm contained an additional sampling probe for collection of duplicate and sorbent cartridge samples. A diagram depicting how the meteorological sensors were mounted is shown in Figure 3-2. The mast was supported by a mount consisting of two side panels positioned at right angles and a support of angle iron seven feet in height which was bolted to the vertex of the side panels. One side panel housed the meteorological translator system which consisted of six temperature translators and six wind speed translators. The translator output was processed with a Data Acquisition/ Reduction Terminal (DART II) and printer/plotter. The DART computer, printer, terminal panel, 12-volt batteries and a power inverter were rack mounted in the center of the boat, as shown in Figure 3-3. A block diagram of the entire assembly, including the organic sampling system, is presented in Figure 3-4.

METEOROLOGICAL MEASUREMENTS

The meteorological system consisted of six temperature sensors with translators, six wind speed sensors and one wind direction sensor with translators, a Psychro-Dyne humidity indicator and associated cables.

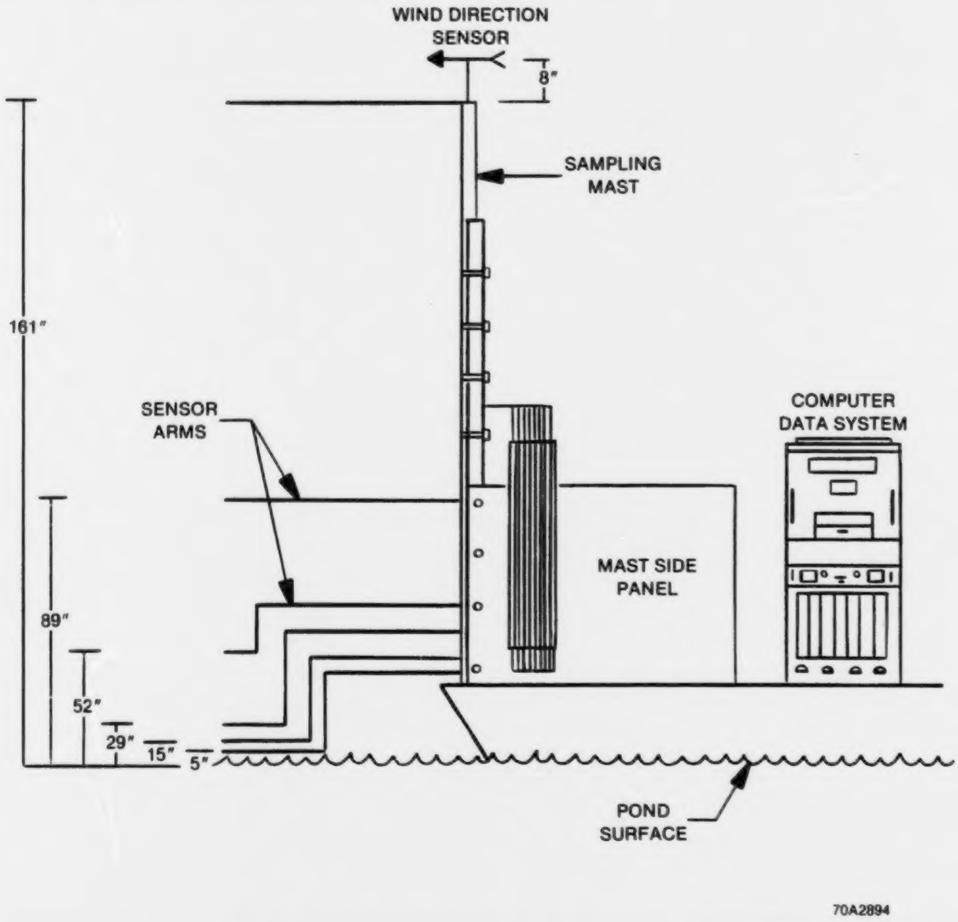

WIND DIRECTION
SENSOR
8"
SAMPLING
MAST
161"
SENSOR
ARMS
COMPUTER
DATA SYSTEM
MAST SIDE
PANEL
89"
52"
29"
15"
5"
POND
SURFACE
70A2894

Figure 3-1. Mast sample collection system.

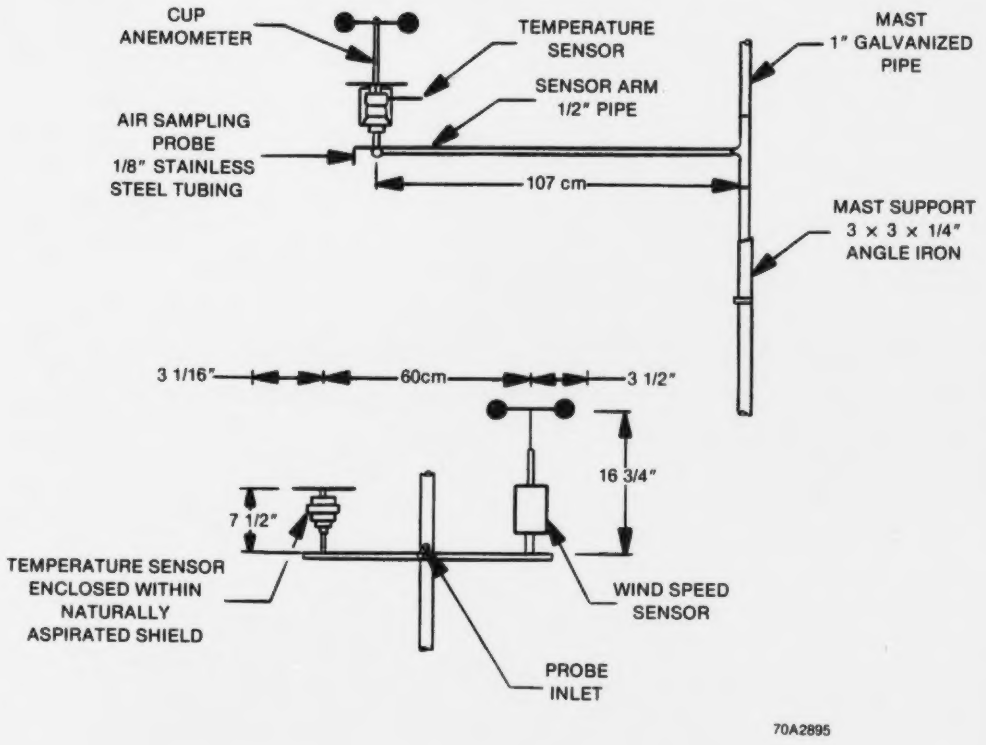

CUP ANEMOMETER
TEMPERATURE SENSOR
MAST 1" GALVANIZED PIPE
SENSOR ARM 1/2" PIPE
AIR SAMPLING PROBE 1/8" STAINLESS STEEL TUBING
107 cm
MAST SUPPORT 3 × 3 × 1/4" ANGLE IRON
3 1/16"
60cm
3 1/2"
16 3/4"
7 1/2"
TEMPERATURE SENSOR ENCLOSED WITHIN NATURALLY ASPIRATED SHIELD
WIND SPEED SENSOR
PROBE INLET
70A2895

Figure 3-2. Sensor mounting diagram.

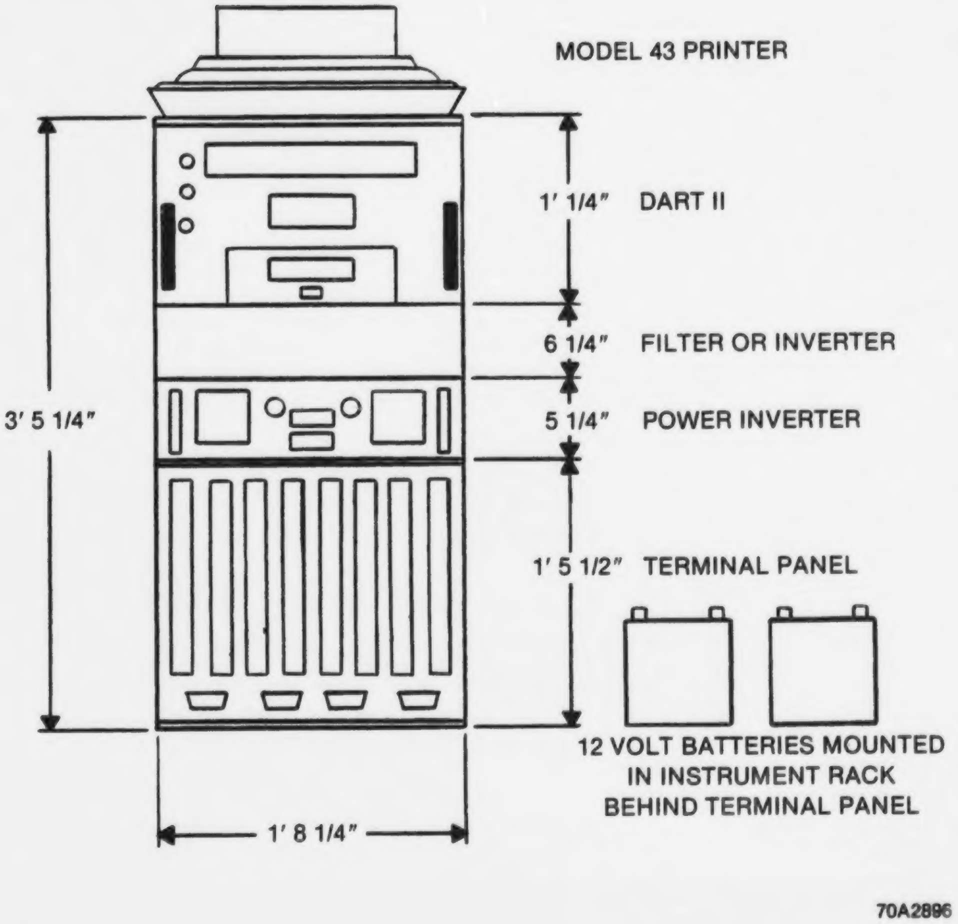

MODEL 43 PRINTER
1' 1/4" DART II
6 1/4" FILTER OR INVERTER
5 1/4" POWER INVERTER
3' 5 1/4"
1' 5 1/2" TERMINAL PANEL
12 VOLT BATTERIES MOUNTED IN INSTRUMENT RACK BEHIND TERMINAL PANEL
1' 8 1/4"
70A2896

Figure 3-3. Rack-mounted instrumentation diagram.

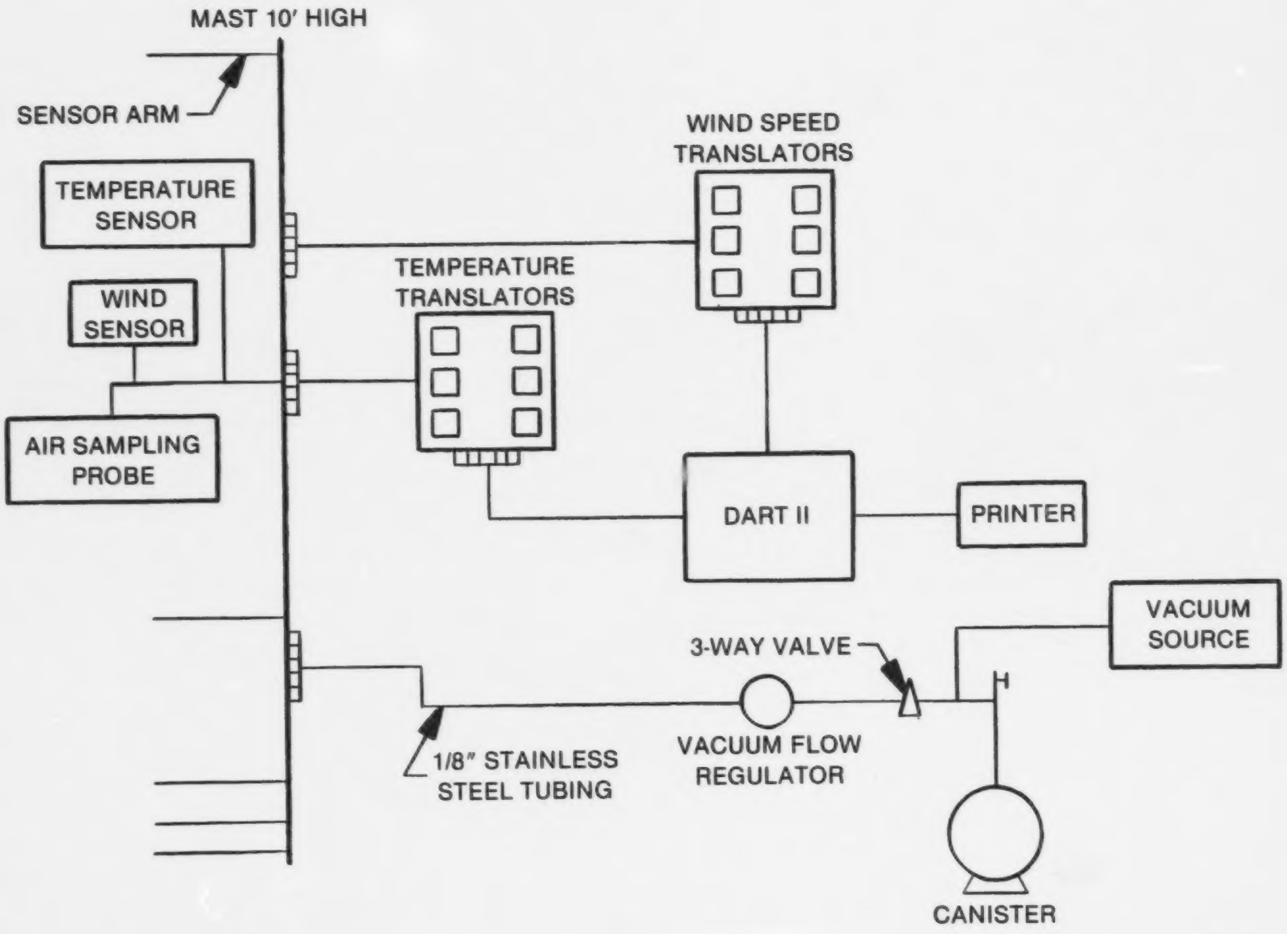

MAST 10′ HIGH
SENSOR ARM
TEMPERATURE SENSOR
WIND SENSOR
AIR SAMPLING PROBE
TEMPERATURE TRANSLATORS
WIND SPEED TRANSLATORS
DART II
PRINTER
VACUUM SOURCE
3-WAY VALVE
1/8″ STAINLESS STEEL TUBING
VACUUM FLOW REGULATOR
CANISTER

Figure 3-4. System block diagram.

70A2897

Temperature

All temperature probes were enclosed in naturally-aspirated radiation shields. The sensing element was a thermistor device, specifically constructed to produce a linear resistance change with temperature. This change in resistance was converted by the temperature translator with an analog 0-1 volt signal representing ambient temperature. Rated acuracy of the probe was ±0.15°C. Water temperature was measured with a mercury thermometer, accurate to ±0.5°F.

Wind Speed

Wind speed was measured using 3-cup anemometer assemblies. A frequency modulated output signal, proportional to wind speed, was received by the translator and converted to a 0-1 volt output. Rated accuracy was ±1% or 0.15 mph, whichever was greater.

Wind Direction

Wind direction was measured using a lightweight vane rotating on a stainless steel shaft. The wind direction translator provided a reference voltage to a low torque potentiometer. Since the wiper arm of the potentiometer was driven by the wind vane sensor, voltage from the wiper was proportional to wind direction. Rated accuracy was ±0.5% or ±1.8 degrees.

Humidity

Relative humidity was measured using a Psychro-Dyne humidity indicator referenced to an NBS traceable psychrometer. The indicator used a small motor-driven fan which provides a constant stream of air across a wet bulb thermometer. Relative humidity was calculated from the difference in temperature readings of the wet bulb thermometer and an adjacent dry bulb thermometer.

Data Processing

Electrical signals from the meteorological translators were processed with an on-board computer, the DART II. A total of 13 channels of data (6 temperature, 6 wind speed and 1 wind direction) were continuously processed by the DART. Each channel was sampled for an instantaneous value every one second. At site FB, these values were averaged and reported every 120 seconds. Because of the effects of humidity and dust on the computer disk loading system at site TB, a default averaging value of 100 seconds was used. At both sites, data for every 10 time intervals were averaged. This corresponded to 20-minute averages of all meteorological conditions at site FB, and 16-minute averages at site TB. Since the air sampling period was 20 minutes at both sites, additional 100-second averages were obtained at site TB, and 20-minute averages were calculated manually.

For each averaging period, the DART calculated additional meteorological parameters which were used for quality control and as a measure of the meteorological variability over the sampling period. These parameters dealt with wind speed and direction, and were intended to demonstrate overall movement of the air mass. The wind parameters which were provided by the DART were:

- average wind speed - 6 heights,
- maximum wind gust - 4 m,
- average wind direction - 4 m,
- wind directon variance,
- vector wind direction, and
- vector wind magnitude.

Average wind speeds were the averages of one-second scalar wind speeds collected at the six sampling heights. The maximum wind gust was the highest one-second wind speed value recorded at the top sampling position (approximately 4 m). Wind gustiness was one quality control criterion used to determine whether or not sampling could be conducted.

The average wind direction was the scalar average of one-second wind directions values recorded 4 m above the water surface. The wind direction variance was calculated as the statistical variance of the one-second wind direction values. The square root of this value was calculated to provide the standard deviation of the wind direction. This provided a measure of how constant the direction of air movement was and was used as a quality control criterion. Vector wind direction and vector wind magnitude are more accurate than scalar averages in representing actual displacement of air during the averaging period, especially with light and variable winds. These measurements were used to determine the amount of air displacement over the body of water.

AMBIENT AIR COLLECTION TECHNIQUES

Air samples were collected in evacuated stainless steel canisters and on solid sorbent traps. Before sampling, each canister was cleaned, evacuated, and the absolute pressure was recorded. The ambient air collection system is shown in Figure 3-5. The canisters were positioned aboard the boat and connected to the different sampling probes by means of 1/8-inch o.d. stainless steel tubing. Stainless steel filters were used as sample probes to remove particulate material. The filters were positioned vertically, with air entering through the bottom side. Vacuum flow regulators were used to provide a constant sampling flow over the 20-minute sampling period. The flow was set prior to sample collection by means of a three-way bypass valve, calibrated flow meters and a regulated vacuum system. The remainder of the system shown in Figure 3-5 was an ultra high purity (UHP) air supply for back-purging the system with clean air.

After sample collection was completed, the canister input valves were closed and the canisters were disconnected from sample lines. The asolute canister pressure was again measured. Prior to shipment, all canister valves were tightened and stem nuts were sealed with Swagelok® plugs. When received at Radian's Austin laboratories, canisters were pressurized with UHP N_2 to

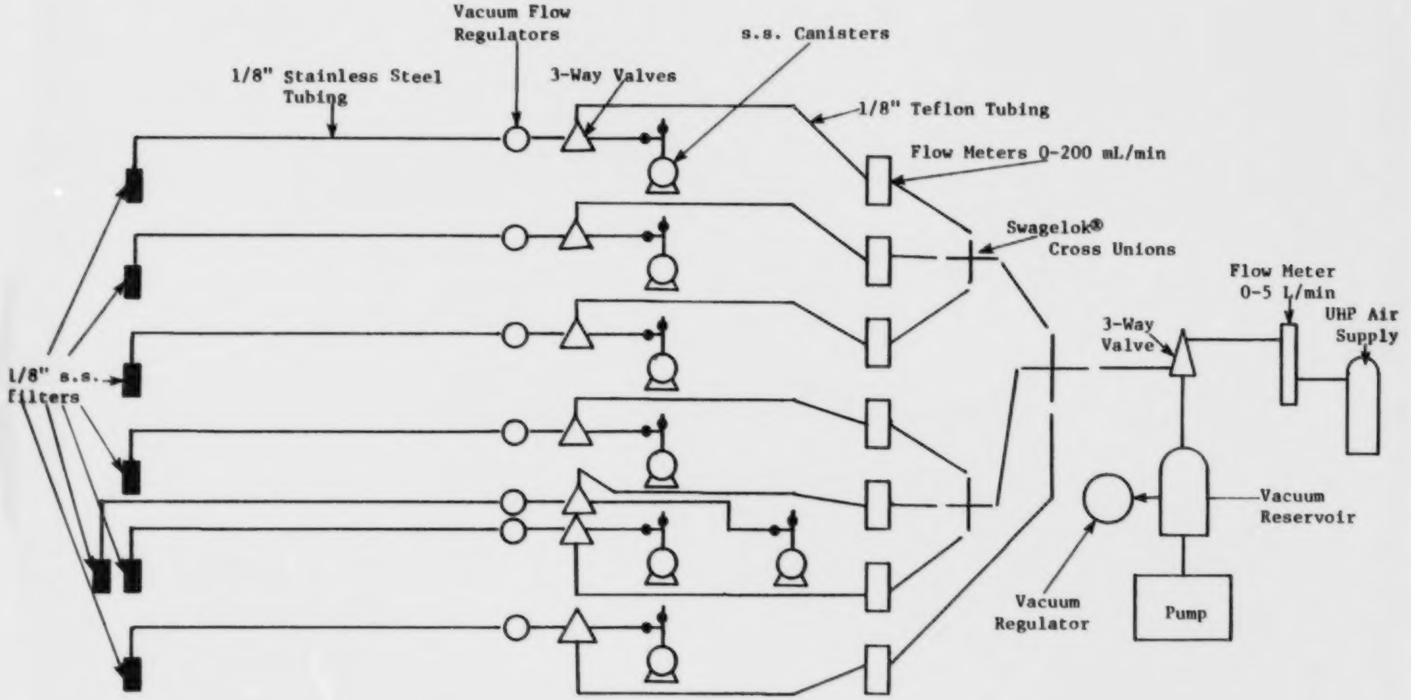

Vacuum Flow Regulators
s.s. Canisters
1/8" Stainless Steel Tubing
3-Way Valves
1/8" Teflon Tubing
Flow Meters 0-200 mL/min
Swagelok® Cross Unions
Flow Meter 0-5 L/min
UHP Air Supply
3-Way Valve
1/8" s.s. filters
Vacuum Reservoir
Vacuum Regulator
Pump

Figure 3-5. Ambient air collection system.

10-15 psig and the final pressure was measured and reported. Nitrogen was added to the canisters to provide positive pressure for removing the sample and to dilute oxygen and moisture in the sample to minimize sample component reactions. The canister dilution was calculated as follows:

$$D = \frac{P_S - P_I}{P_T}$$

where:

P_S = absolute canister pressure after sample collection,
P_I = initial absolute canister pressure, and
P_T = final absolute pressure after addition of UHP N_2.

The duplicate sampling arm (#2) was also used to collect sorbent cartridge samples. A diagram of the sorbent cartridge collection system is presented in Figure 3-6. The volume of air pulled through the cartridge was determined by measuring the pressure differential of a fixed volume sample reservoir with a high precision vacuum gauge.

After the sorbent cartridge sampling line had been purged, the three-way valve was switched to the sample position and the pressure of the 2.8 L sample reservoir was measured and recorded. The vacuum flow regulator was set to a flow of 50 mL/min, which provided a sample volume of 1.0 L. After the integration period, the final pressure of the 2.8 L sample reservoir was measured and the volume of air passed through the tube was calculated as:

$$Vg = \frac{(P_F - P_I)}{14.7} \quad (2.8\ \text{L})$$

where:

P_F = reservoir pressure at completion of sampling and
P_I = initial reservoir pressure.

The sampling system used to collect upwind air samples is shown in Figure 3-7. It was similar to the systems which were used on the sampling mast, except that a single evacuated cylinder was used for the purge instead of a pump, since electricity was not available. The samples were collected three meters above pond level by means of 1/8-inch stainless steel tubing and a stainless steel sampling probe. The probe was supported by 1-inch polypropylene pipe tubing.

WATER COLLECTION TECHNIQUES

Water samples were collected approximately six inches below the pond surface in 40 mL screwcap glass vials with Teflon® liners. Water samples were collected during the 20-minute air collection period at a point as close

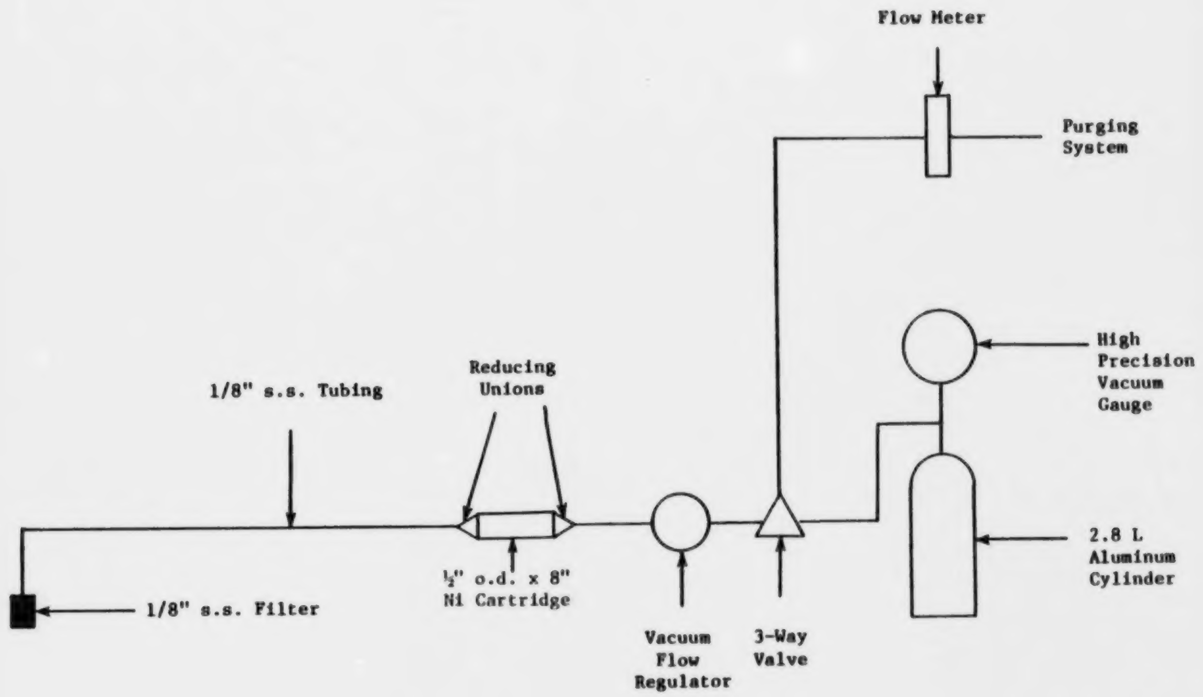

Flow Meter
Purging System
High Precision Vacuum Gauge
1/8" s.s. Tubing
Reducing Unions
2.8 L Aluminum Cylinder
1/8" s.s. Filter
½" o.d. x 8" Ni Cartridge
Vacuum Flow Regulator
3-Way Valve

Figure 3-6. Sorbent cartridge collection system.

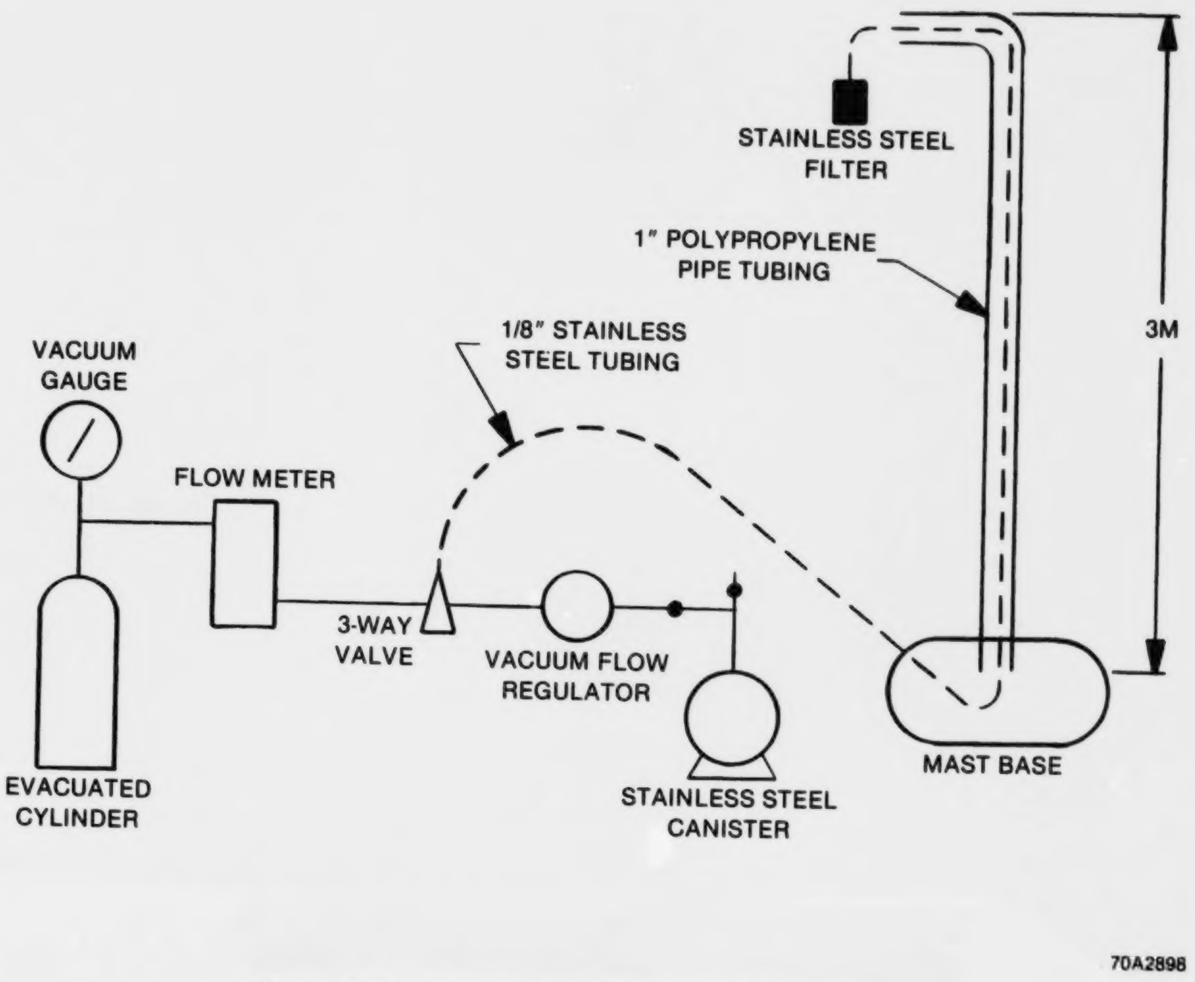

VACUUM GAUGE
EVACUATED CYLINDER
FLOW METER
3-WAY VALVE
1/8" STAINLESS STEEL TUBING
VACUUM FLOW REGULATOR
STAINLESS STEEL CANISTER
STAINLESS STEEL FILTER
1" POLYPROPYLENE PIPE TUBING
3M
MAST BASE
70A2898

Figure 3-7. Upwind air sample collection system.

as possible to the sample probes. The samples were stored between 0°C and 5°C from the time they were collected until the time they were analyzed. Water samples were also collected approximately six feet from the shoreline near the inlet, outlet and sides of the ponds.

FIELD SAMPLING PROCEDURES

Sample collection procedures involved assembling all equipment onboard the boat, positioning the boat in the pond, determining presampling meteorological conditions and the actual sample collection procedure. Strict quality control guidelines were used to determine the boat position and meteorological conditions necessary to allow sampling.

Boat Positioning

After the boat was placed in the water at each site, the sample collection system was assembled onboard. When all sampling and safety equipment had been assembled and checked out, the boat was launched. Positioning of the boat for sample collection satisfied the following criteria:

- Distance from obstacles: The location selected for Concentration-Profile testing must be at least 50 (and preferably 200) times the distance of the height of the dike or other significant obstacle away from the edge of the pond along the direction of average wind. Profile measurements taken closer than this cannot reflect the log profile assumed in the methodology and, consequently, the emissions data will not be valid.

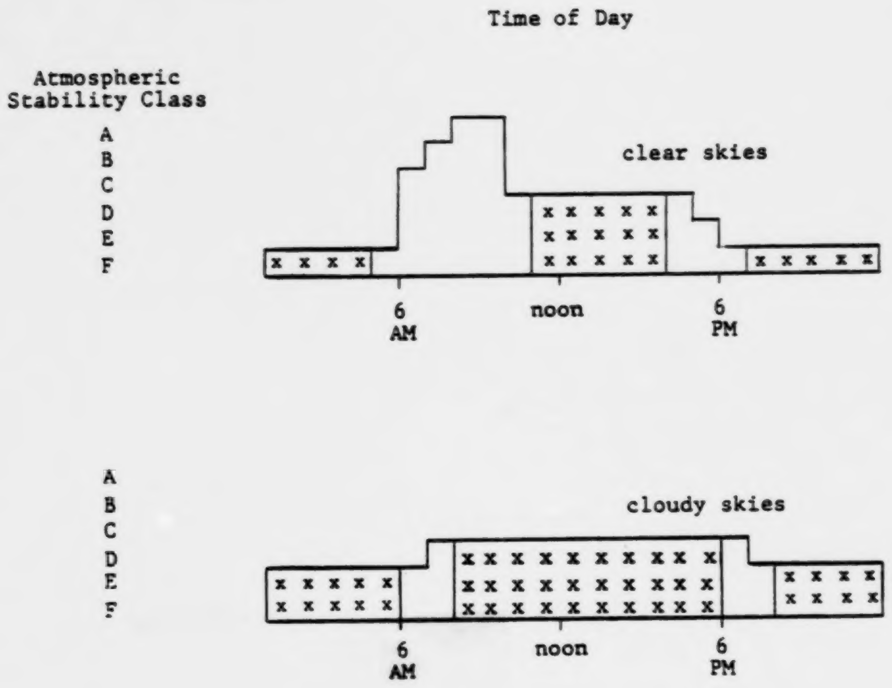
- The boat should be pointed directly into the wind to allow minimum disturbance to windflow.

- The boat should be as secure as possible to prevent rotation and rocking motions which would cause the sampling heights to vary.

Presampling Meteorological Considerations

To properly fit the C-P technique, data must be collected during proper atmospheric conditions. Ideally, all data would be collected under conditions of maximum atmospheric stability. The proper sampling times for different atmospheric stability conditions, defined by Pesquill stability classes, are presented in Figure 3-8. According to the Pesquill classification, atmospheric stability can range from class A, which is least stable, to class F, which is most stable. In this figure, an "x" indicates proper sampling periods. This figure is somewhat misleading since atmospheric stability classes E and F rarely, if ever, occur during the day.

Several methods of measuring atmospheric stability are available (9). For this project, a series of four criteria were used to define atmospheric stability. The first is described in Table 3-1 and consisted of manual inspection of atmospheric conditions to determine stability. If the proper stability criteria were not met, sampling preparations were not initiated.



"x" indicates acceptable measurement period

Figure 3-8. Acceptable sampling periods for clear and cloudy conditions.

TABLE 3-1. KEY TO STABILITY CATEGORIES

Surface Wind Speed (at 10 m), m. sec^{-1}	Day			Night	
	Incoming Solar Radiation				
	Strong	Moderate	Slight	Thinly Overcast or $\geq$ 4/8 Low Cloud	$\leq$ 3/8 Cloud
$<$ 2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
$>$ 6	C	D	D	D	D

The neutral class, D, should be assumed for overcast conditions during day or night.

Class A is the most unstable, class F the most stable class considered here. Night refers to the period from one hour before sunset to one hour after sunrise. Note that the neutral class, D, can be assumed for overcast conditions during day or night, regardless of wind speed.

"Strong" incoming solar radiation corresponds to a solar altitude greater than 60° with clear skies; "slight" isolation corresponds to a solar altitude from 15° to 35° with clear skies. Table 170, Solar Altitude and Azimuth, in the Smithsonian Meteorological tables (List, 1951) can be used in determining the solar altitude. Cloudiness will decrease incoming solar radiation and should be considered along with solar altitude in determining solar radiation. Incoming radiation that would be strong with clear skies can be expected to be reduced to moderate with broken (5/8 to 7/8 cloud cover) middle clouds and to slight with broken low clouds.

If manual inspection of atmospheric conditions demonstrated that proper conditions existed, then sampling preparations were initiated.

Prior to sampling, meteorological data were collected for a 20-minute period and used for further checks of proper atmospheric stability. This was necessary to assure a relatively constant wind speed and direction, and atmospheric stability. The meteorological criteria used to determine if sampling could be performed were:

- The mean wind speed for the 20-minute period must be greater than 5 mph.
- The maximum wind speed (gust) must not be greater than three times the mean wind speed.
- The wind direction standard deviation (WSD) must not be greater than 45°.
- The Richardson (R_i) number must be greater than -0.1.

The Richardson number is the parameter which was used to define the atmospheric stability classes shown in Table 3-1. It is based on the ratio of temperature gradient with respect to wind gradient and is defined as:

$$R_i = \frac{g(T_2 - T_1) / (Y_2 - Y_1)}{T_1[(u_2 - u_1) / (Y_2 - Y_1)]^2}$$

where:

R_i = Richardson number,
g = acceleraton of gravity,
T_1 = absolute temperature at height Y_1,
T_2 = absolute temperature at height Y_2, and
u_2, u_1 = wind velocities at heights Y_2 and Y_1.

The Richardson number relates to atmospheric stability using the criteria presented in Table 3-2.

Because sampling schedule requirements did not allow sufficient time to consider all data points for calculating Richardson numbers in the field, two data points (heights 1 and 6) were used to perform the calculation during sampling.

Sampling System Purge

During collection of presampling meteorological data, the air sampling system was purged and checked for proper flow rates. This was accomplished by placing all three-way valves in the bypass position, thus connecting the sampling probes to a vacuum reservoir. The vacuum reservoir was maintained

TABLE 3-2. CORRELATION OF RICHARDSON NUMBER (R_i) WITH PESQUILL STABILITY CLASS

Atmospheric Stability Class	R_i
A	< -1.2
B	-1.2 to -0.43
C	-0.43 to -0.1
D	-0.1 to 0.05 (note for neutral stability $R_i = 0$)
E	0.05 to 0.10
F	> 0.10

at 6 psia by means of a pump and a vacuum regulator. This allowed purging of all lines with ambient air. The flow rate of each line was monitored on a bank of seven flow meters which were calibrated at 6 psia. If flow adjustments were required, they were made at that time. The 2.8 L stainless steel canisters normally used by Radian for ambient air sampling required a flow rate of 115 mL/min to provide a 20-minute integrated sample and the 1.0 L EPA canisters required a flow rate of 40 mL/min.

Sampling Operations

During each 20-minute sampling period, temperature and wind speed data were collected at six heights and wind direction data were collected at one height. The sampling rates and averaging times for these data have been described. Air sample collection was initiated by rotating the three-way valves to the sample position and opening the canister shutoff valves. One canister sample was collected at each of the six sampling heights. The extra probe on sample arm #2 was used to collect a duplicate canister sample or a sorbent cartridge sample. Also, one humidity measurement, at least one water temperature measurement, and one water sample were collected during each run.

After the 20-minute collection period was completed, all canister valves were closed and the canisters were sealed, labeled and logged. The three-way valves were returned to the purge position and the UHP air was pumped in reverse through the system to clean the sample lines and regulators.

SECTION 4

ANALYTICAL METHODS

The analyses of air and water samples were performed using a cryogenic concentration technique, followed by gas chromatographic (GC) separation of VOC species. A dual detector GC technique using simultaneous photoionization (PID) and flame ionization (FID) detectors was used for species identification and quantitation. Species identifications for the water samples were confirmed by gas chromatographic/mass spectrometric (GC/MS) analysis. The analytical methods and data reduction techniques used for GC analyses are presented below, followed by the presentation of GC/MS analytical methods.

GC/FID/PID ANALYSIS OF AIR AND WATER SAMPLES

A schematic diagram of the analytical system which was used in this work is presented in Figure 4-1. The system was designed to accept air samples collected in pressurized canisters or on solid sorbents (via thermal desorption), and water samples via a purge and cryotrap technique. Analyses were performed in three basic steps: cryogenic concentration, chromatographic separation and detection by PID and FID, and quantitative and qualitative data reduction. The analytical methods and GC/PID/FID analysis are described below.

Cryogenic Concentration

The cryogenic concentration procedure involved separation of VOC species from the collection matrix, removal of moisture, cryogenic focusing, and measurement of the sample volume analyzed.

Species Separation from Sample Matrices--

Techniques for separation of VOC species from the collection matrix differed with the sample type. The techniques used for each matrix were:

- Water Samples — A 0.1 mL - 3.0 mL sample aliquot was placed in a Bellar purge tube and diluted to 5 mL with deionized-distilled water. For samples which foamed, approximately 1 g NaCl (cleaned by heating to 400°C) was added. The sample was then purged with ultra high purity (UHP) nitrogen (N_2) at a rate of 40 mL/min for 10 minutes.

- Sorbent Cartridges — Sorbent cartridges were purged with 50 mL UHP N_2 to remove oxygen. They were then heated to 275°C and purged with 1 L of UHP N_2 at a rate of 100 mL/min.

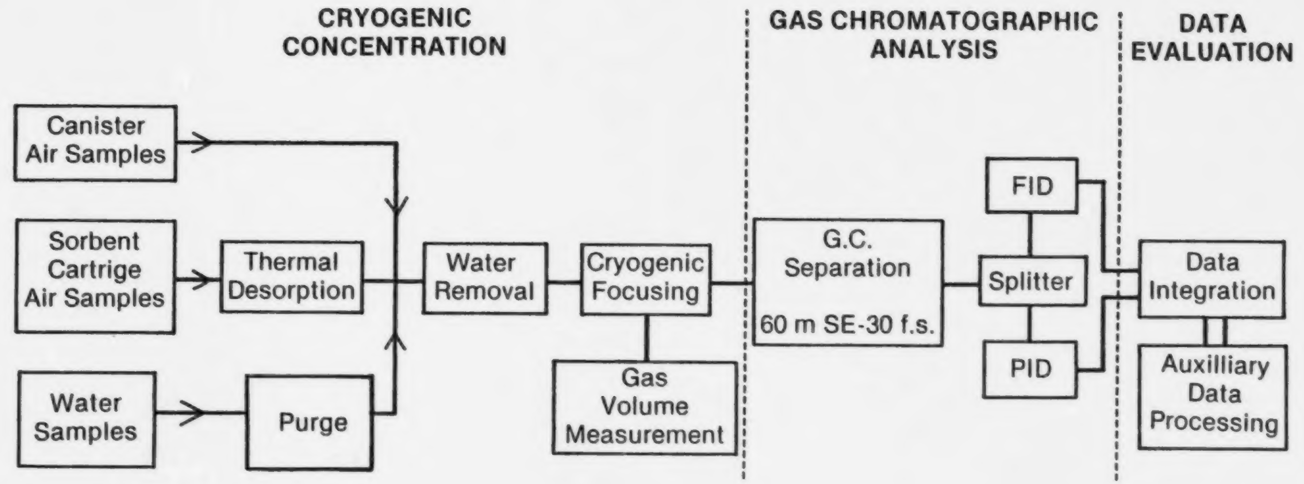

CRYOGENIC CONCENTRATION
GAS CHROMATOGRAPHIC ANALYSIS
DATA EVALUATION
Canister Air Samples
Sorbent Cartrige Air Samples
Water Samples
Thermal Desorption
Purge
Water Removal
Cryogenic Focusing
Gas Volume Measurement
G.C. Separation
60 m SE-30 f.s.
FID
Splitter
PID
Data Integration
Auxilliary Data Processing

Figure 4-1. Analytical system overview.

• Canister Samples	Air samples in pressurized canisters were transferred directly into the moisture removal device.

Moisture Removal--

After separation from the collection matrix, the organic vapors were passed through a single tube Perma Pure® drier for removal of moisture. The Perma Pure drier consisted of a semipermeable tube (24 in for air and 48 in for water samples) encased in 1/8 inch o.d. tube which was purged with UHP air (<0.1 ppmv-C TNMHC, <3 ppm H_2O) at a rate of 1000 mL/min. Between sample applications, the outer tube was heated to 60°C while purging the interior tube with UHP N_2 to eliminate sample memory.

The effects of the Perma Pure drier on the recoveries of organic vapors in the sample stream were evaluated for a variety of VOC species and classes prior to selection of a drying method. The recoveries of different classes of organic vapors using a 48-inch Perma Pure drier and a K_2CO_3 solid desiccant are presented in Table 4-1. More specific data on individual organic species are presented in Reference 8. Efficient recoveries (>85%) using the Perma Pure drier were demonstrated for aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons and aldehydes. The K_2CO_3 solid desiccant functioned well for aliphatic hydrocarbons but retained the heavier aromatic species and some chlorinated hydrocarbons. Neither system functioned well for ketones and alcohols. The ketone efficiencies for the Perma Pure drier varied with the age of the drier. As the drier aged, recovery efficiencies increased from 0% to approximately 70%.

Cryogenic Trapping--

After passing through the Perma Pure drier, the sample stream passed through a 6 inch by 1/8 inch o.d. nickel tube packed with 80/100 mesh glass beads and cooled in liquid oxygen. All VOC species with the exception of methane were trapped. VOC species were thermally desorbed by immersing the trap in boiling water, followed by heating to approximately 180°C with an electrical heating element. During desorption, the trap was backflushed with UHP helium to inject the organic species onto the GC capillary column as a discrete plug. The efficiency of glass bead traps for collecting eight hydrocarbon species has previously been evaluated (10).

Sample Volume Determination--

The quantity of gas passed through the trap was determined by collecting the trap effluent in a fixed volume reservoir and measuring the pressure of the reservoir with a high precision gauge (Wallace and Tierman Model 61C-1A-0015). The reservoir (3.4 L) was initially evacuated to approximately 2.0 psia and the effluent was then collected in the reservoir. Exact pressure readings were taken before and after effluent collection. The volume of gas which was passed through the cryogenic trap was calculated as the dry gas volume since moisture was removed prior to volume measurement. The equation used for volume calculations is discussed below.

TABLE 4-1. SUMMARY OF ORGANIC VAPOR RECOVERIES USING K_2CO_3 AND PERMA PURE® DRIERS

Class	Carbon Number Range	Concentration Range (ppbv-C)	Number Species Tested	Recovery Perma Pure (%)	Recovery K_2CO_3 (%)
Alkanes	2 - 10	16 - 280	19	92 - 106	83 - 102
Alkenes	2 - 5	141 - 204	8	100 - 101	98 - 100
Aromatics	6 - 10	167 - 505	12	90 - 99	20 - 94
Chlorinated Hydrocarbons	1 - 6	66 - 206	6	99 - 104	16 - 83
Aldehydes	2 - 5	140 - 1400	6	84 - 95	0 - 6
Ketones	3 - 5	28 - 66	4	0 - 70[1]	0 - 10
Alcohols	1 - 4	25 - 1500	5	0	0

[1] Change in drier permeability observed.

VOC Species Separation and Determination by Gas Chromatography

The analytical methods used for separation of the VOC species and the use of dual PID/FID detection for VOC species determination are discussed below.

Gas Chromatographic Instrumentation and Analytical Parameters--

The instrumentation and analytical parameters used for the GC/PID/FID analyses were:

- Instrument: Varian 3700 GC/PID/FID with subambient programming.
- PID: HNU Model 52 with 10.0 eV lamp.
- Analytical Column: 60 m, SE-30, wide bore, thin film, fused silica.
- Oven Program: -50°C for 2 min; 6°C/min to 100°C.
- Carrier Gas: UHP He at 2 mL/min and 19 psi.
- Makeup Gas: UHP N_2 at 30 mL/min (PID and FID).

Simultaneous use of the PID and FID required operating the two detectors in a manner which would not sacrifice chromatographic resolution or detector sensitivity. Since the PID was more sensitive than the FID, it was possible to operate the detectors in parallel by splitting a small portion of the chromatographic column effluent to the PID, without a significant sacrifice in FID sensitivity. Parallel as opposed to serial operation allowed superior resolution. The splitter (Scientific Glass Engineering) consisted of a short piece of 0.4 mm i.d. glass-lined stainless steel tubing, silver soldered into a low dead volume union. Two lengths of 0.22 mm i.d. fused silica tubing were glued into a two-hole graphitized-vespel ferrule which butted against one end of the glass-lined tubing. The analytical column was inserted through the glass-lined tubing and butted against the two-hole ferrule. The ratio of flow to each detector was controlled by adjusting the lengths of splitter tubing.

Dual Detector Species Determination--

Example chromatograms using simultaneous PID and FID detection for a 38-component hydrocarbon mixture are presented in Figure 4-2. To facilitate labeling, alkenes and aromatics are labeled on the PID (upper) chromatogram and alkanes are labeled on the FID (lower) chromatogram. Example chromatograms of the analysis of a standard mixture containing chlorinated and aromatic hydrocarbons in water are presented in Figure 4-3.

Since the FID responds to molecules based on the number of carbon atoms, while the PID response is roughly based on the degree of unsaturation, the ratio between the two detectors can be used as a tool in identifying chromatographic peaks. Relative detector responses for organic species were

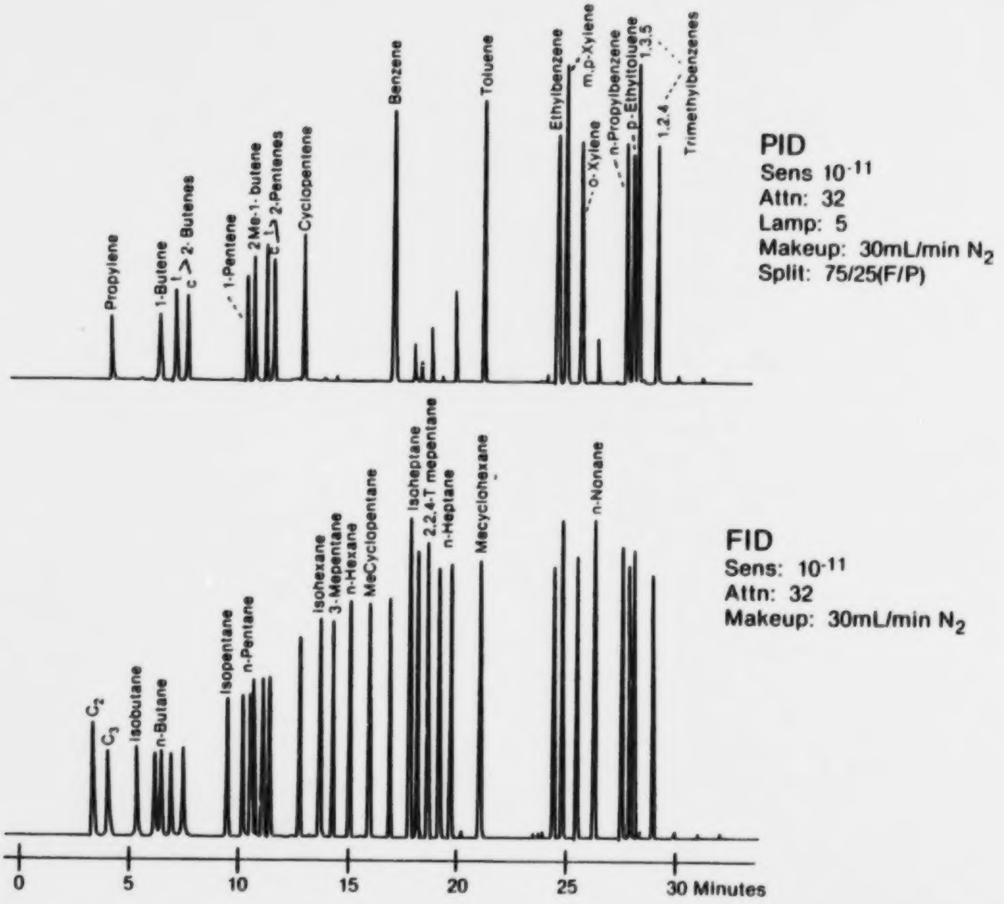


Figure 4-2. Analysis of a 38-component hydrocarbon standard by the Cryogenic GC/PID/FID Technique.

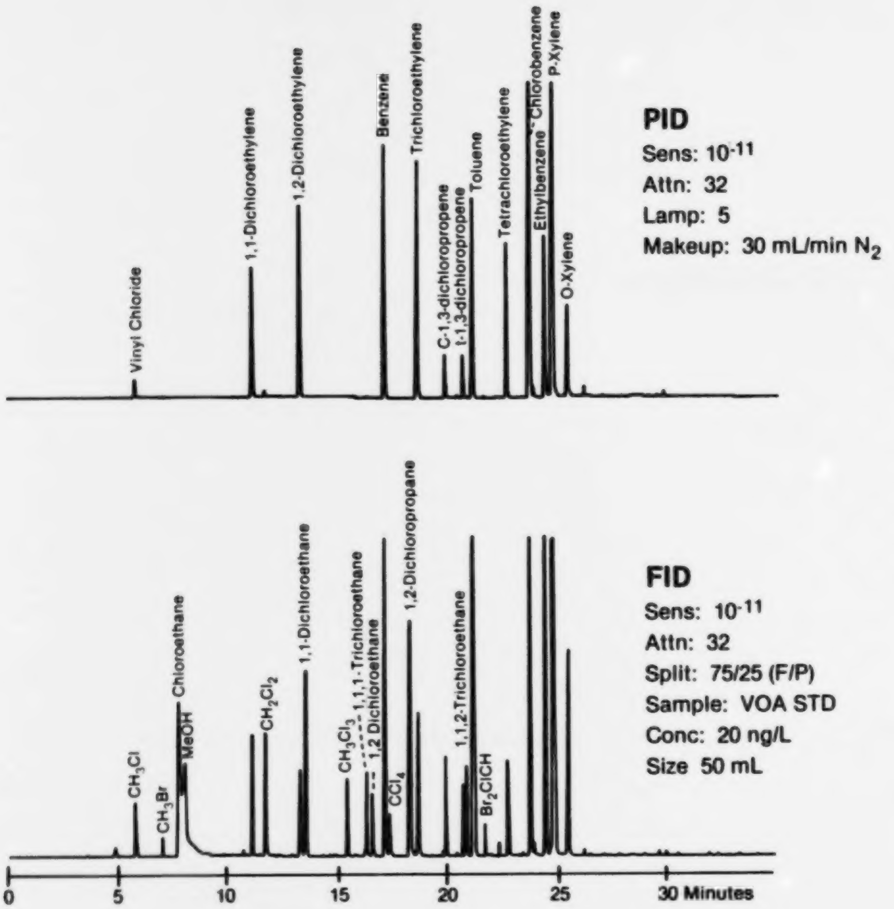


Figure 4-3. Analysis of water spiked with chlorinated and aromatic hydrocarbons using the Purge-and-Cryotrap GC/PID/FID Technique.

obtained by ratioing results between the two detectors. The effects of detector fluctuations were minimized by normalizing all response ratios to the response ratio for a single compound. Toluene was chosen as the normalizing compound since it gave a good response on both detectors and a review of the literature along with previous experimental data indicated that toluene is normally present in ambient air. Toluene normalized responses (TNR) for the PID and FID detectors were calculated using the following equation:

$$\mathrm{TNR} = \frac{\mathrm{PR_x} \cdot \mathrm{FR_t}}{\mathrm{FR_x} \cdot \mathrm{PR_t}} \times 100$$

where PR_x and PR_t are PID responses for organic species x and toluene, respectively, and FR_x and FR_t are FID responses for species x and toluene, respectively. By definition, toluene will always have a value of 100.

An additional goal of this work was to determine chemical classes when species identifications could not be established. These data were then used in conjunction with GC/MS data to provide species identifications. TNR data were averaged for all species listed in Table 4-2 within each class eluting before and after 17 minutes. This time was chosen because all aromatics elute later, and because TNR values for alkenes decreased as the carbon number (and retention time) of the compound increased. Average data for organic classes are presented in Table 4-3.

Sample components which could not be identified as individual species were placed into chemical classes on the basis of their measured TNR values and the class TNR averages presented in Table 4-3. For classification of unidentified sample components, the 17 minute elution time differentiation was used, but only the alkane, alkene, aromatic, and chlorinated chemical classes were considered. Other classes such as aldehydes, ketones, alkynes and sulfur containing organics were not considered unless individual species identifications were possible. All unidentified peaks were classified as either alkanes, alkenes, aromatics or chlorinated hydrocarbons. For alkanes, alkenes and aromatics, unidentified compounds were also classified by carbon number, such as "UNID C_6 Alkane". The carbon number classifications were based on elution order of standards in the C_6 - C_{10} range. This type of classification facilitated comparisons with GC/MS data, and summation of chemical class concentrations.

Data Evaluation

Chromatographic data were processed using a data system consisting of a Varian Vista 401 Chromatography Data System (401 CDS) interfaced to an Apple II Plus micro-computer. The 401 CDS integrated all peak areas, stored raw data on floppy disks, performed peak identification against preset peak tables, performed quantitative peak evaluation against external standard calibrations, and provided a simultaneous hard copy plot for each detector and a hard copy report for each chromatogram. These reports were used as a routine quality control check for the Apple II. The 401 CDS transmitted

TABLE 4-2. RETENTION TIMES AND NORMALIZED PID/FID RESPONSES FOR HYDROCARBON SPECIES

Compound	Retention Time (min)	TNR	Compound	Retention Time (min)	TNR
			Alkanes		
Ethane	3.30	0	Cyclohexane	17.35	25
Propane	4.02	0	Isoheptane	17.94	8
Isobutane	5.38	0	2,3-Dimethylpentane	17.94	10
n-Butane	6.50	0	3-Methylhexane	18.26	8
Neopentane	7.14	2	2,2,4-Trimethylpentane	18.72	18
Isopentane	9.55	2	n-Heptane	19.25	7
n-Pentane	10.76	2	Methylcyclohexane	19.78	36
Neohexane	12.21	4	2,5-Dimethylhexane	20.44	16
Cyclopentane	13.30	2	2,3,4-Trimethylpentane	21.03	33
2,3-Dimethylbutane	13.55	7	3-Methylheptane	21.96	17
Isohexane	13.82	5	2,2,5-Trimethylhexane	22.36	21
3-Methylpentane	14.39	5	n-Octane	22.93	8
n-Hexane	15.15	4	n-Nonane	26.35	14
Methylcyclopentane	16.08	4	n-Decane	29.80	16
2,4-Dimethylpentane	16.39	9	n-Undecane	34.38	15
			Alkenes, Dienes, and Alkynes		
Ethylene	3.30	0	2-Ethyl-1-butene	15.11	65
Acetylene	3.30	0	t-2-Hexene	15.43	67
Propylene	4.02	72	c-2-Hexene	15.76	69
Propyne	4.60	2	c-3-Methly-2-pentene	16.00	70
1-Butene	6.24	65	Methylcycolopentene	17.07	73
Isobutene	6.24	79	Cyclohexene	17.98	58
1,3-Butadiene	6.36	104	1-Heptene	18.81	49
t-2-Butene	6.95	78	3-Heptene	19.19	51
1-Butyne	7.27	7	2-Heptene	19.27	57
c-2-Butene	7.50	70	2,4,4-Trimethyl-1-pentene	19.57	55
3-Methyl-1-butene	8.73	65	2,4,4-Trimethyl-2-pentene	20.27	50

(Continued)

TABLE 4-2. (Continued)

Compound	Retention Time (min)	TNR	Compound	Retention Time (min)	TNR
1-Pentene	10.26	64	1-Methylcyclohexene	21.51	60
2-Butyne	10.31		3,5,5-Trimethyl-1-hexene	21.70	57
2-Methyl-1-butene	10.61	73	2-Ethyl-1-hexene	22.44	57
Isoprene	10.85	89	1-Octene	22.57	44
t-2-Pentene	11.18	77	t-2-Octene	23.06	61
c-2-Pentene	11.45	71	c-2-Octene	23.31	54
2-Methyl-2-butene	11.72	76	1-Nonene	25.95	52
Cyclopentene	12.88	75	4-Nonene	26.19	47
4-Methyl-1-pentene	13.20	59	α-Pinene	27.30	75
c-4-Methyl-2-pentene	13.80	53	β-Pinene	28.65	65
t-4-Methyl-1-pentene	13.95	62	1-Decene	29.35	36
2-Methyl-1-pentene	14.64	65	Limonene	30.60	63
1-Hexene	14.70	59	1-Undecene	33.75	35
			Aromatics		
Benzene	17.02	112	1,3,5-Trimethylbenzene	28.17	117
Toluene	21.13	100	t-Butylbenzene	28.95	61
Ethylbenzene	24.51	87	1,2,4-Trimethylbenzene	29.04	81
p-Xylene	24.83	105	Isobutylbenzene	29.67	66
m-Xylene	24.87	95	1,2,3-Trimethylbenzene	30.09	83
Styrene	25.38	111	Indan	30.47	80
o-Xylene	25.54	77	p-Isopropyltoluene	30.22	80
Isopropylbenzene	26.65	79	m-Diethylbenzene	31.15	73
n-Propylbenzene	27.61	79	n-Butylbenzene	31.53	66
m-Ethyltoluene	27.87		p-Diethylbenzene	31.61	75
p-Ethyltoluene	27.98	79	Naphthalene	38.21	123
			Aldehydes		
Acetaldehyde	5.84	2	Buteraldehyde	14.15	60
Propionaldehyde	9.87	84	Isovaleraldehyde	16.70	66
Isobuteraldehyde	12.78	67	Valeraldehyde	18.35	56

(Continued)

TABLE 4-2. (Continued)

Compound	Retention Time (min)	TNR	Compound	Retention Time (min)	TNR
			Ketones		
Acetone	10.05	160	2-Pentanone	18.09	105
Butanone	14.70	153	3-Pentanone	18.47	141
			Halogenated Alkanes		
Chloromethane	4.80	0	1,2-Dichloroethane	16.42	0
Bromomethane	6.97	0	Tetrachloromethane	17.22	0
Chloroethane	7.73	0	Bromodichloromethane	18.55	0
Trichlorofluoromethane	9.93	0	1,2-Dichloropropane	18.19	0
Dichloromethane	11.71	0	1,1,2-Trichloroethane	20.82	0
1,1-Dichloroethane	13.46	0	Dibromochloromethane	21.68	0
Trichloromethane	15.30	0	1,1,2,2-Tetrachloroethane	25.53	3
1,1,1-Trichloroethane	16.14	0			
			Chlorinated Alkenes and Aromatics		
Vinyl Chloride	5.71	53	Chlorobenzene	23.77	150
1,1-Dichloroethylene	11.12	190	o-Chlorotoluene	27.32	124
t-1,2-Dichloroethylene	13.29	410	m-Chlorotoluene	27.43	135
Trichloroethylene	18.58	300	p-Chlorotoluene	27.50	130
c-1,3-Dichloropropene	19.86	124	m-Dichlorobenzene	29.14	154
t-1,3-Dichloropropene	20.09	129	p-Dichlorobenzene	29.35	155
Tetrachloroethylene	22.76	290	o-Dichlorobenzene	30.18	137
			Sulfur Hydrocarbons		
Carbonyl sulfide	3.62	>1000	Butyl mercaptan	19.06	133
Methyl mercaptan	6.64	650	Tetrahydrothiophene	22.27	185
Ethyl mercaptan	10.23	350			

*Toluene normalized response.

TABLE 4-3. ORGANIC SPECIES CLASS PID/FID NORMALIZED RESPONSES

Class	Retention Times < 17 min.		Retention Times > 17 min.	
	Species Tested	TNR (Mean ± SD)	Species Tested	TNR (Mean ± SD)
Halogenated Alkanes	9	0 ± 0	6	1 ± 1
Simple Alkanes	13	3 ± 3	10	12 ± 4
Cycloalkanes + Trimethylalkanes	2	3 ± 1	5	27 ± 8
Alkynes	3	3 ± 3	0	---
Alkenes	23	70[a] ± 11	20	55 ± 10
Aldehydes	4	69[b] ± 10	1	56
Ketones	2	157 ± 5	2	123 ± 25
Aromatics	0	---	21	87 ± 18
Chlorinated Aromatics	0	---	7	141 ± 12
Chlorinated Alkenes	3	218 ± 180	4	211 ± 97
Sulfur Hydrocarbons	2	500[c] ± 210	2	129 ± 37

[a] Does not include ethylene
[b] Does not include acetaldehyde
[c] Does not include carbonyl sulfide

processed GC data to the Apple II. The Apple II was specifically programmed for the dual detector PID/FID analyses. The primary function of the Apple II was to reprocess data from the 401 CDS and provide a single combined report. Qualitative data processing was performed by the Apple II on a higher level than by the 401 CDS. Quantitative data processing performed by the two systems was similar, but the 401 CDS required more manual input and used different calculations than the Apple II. The Apple II was also programmed to do several special calculations and provide on-line quality control support. Since all final chromatographic data were produced by the Apple II, only these data will be described below.

Qualitative Data Evaluation--

The first function performed by the Apple II was qualitative peak evaluation. This was performed against a peak table stored on the Apple II disk. Retention time data for the Apple II were stored as relative retention times (RRTs) to toluene, although absolute retention times were also reported to facilitate manual data interpretation. Also, each compound was assigned an identification number to facilitate quantitation and to translate processed data to computer disk storage.

Prior to qualitative chromatogram evaluation, toluene was identified by its retention time using a 1% window. Isobutane was then identified by its RRT to toluene using a 3% window. The computer selected the largest peak within each window. A second retention time marker was used because even slight inconsistencies in the injection technique could bias the initial ten minutes of the chromatogram enough to misidentify early eluting compounds if only toluene was used.

Identification of sample components was accomplished by calculating RRTs to toluene for all sample components and comparing these to the peak table. For compounds which eluted prior to 5 minutes, RRTs were adjusted according to the observed offset for isobutane. If isobutane was not observed in the sample then this step was omitted. Each sample component RRT was then compared to the peak table and the closest fitting peak identification (within 1%) was applied to the sample component. If no compound in the peak table matched the sample component RRT to within 1%, then the component was flagged as an unknown and its class was determined on the basis of data presented in Table 4-3. The computer algorithm used for peak identification was presented in the Quality Assurance Project Plan (7).

The Apple II also calculated and printed TNR values for all sample components, whether identified or not. Computer species identifications were checked manually for consistencies with TNR data. When necessary, identifications of sample components were changed or reclassified as unknowns within certain chemical classes.

Quantitative Data Evaluation--

All sample components were quantitated on the basis of FID carbon response relative to propane or n-hexane. All C_2 - C_4 compounds were quantitated against propane and all C_5 - C_{11} compounds were quantitated against n-hexane. A quantitative standard of propane and n-hexane (referenced to NBS SRM propane) was analyzed every morning. For each analysis, the operator entered the initial and final reservoir pressure, the sample dilution factor and the analysis type (standard or sample). The reservoir volume and standard concentrations were used by the Apple II to calculate sample volumes and response factors. The volume of gas was calculated using the following equation:

$$Vg = \frac{(P_2-P_1)}{14.7}\ (3.4\ L)$$

where:

Vg = volume of sample or standard (L)

P_1 = initial reservoir pressure

P_2 = final reservoir pressure

3.4 L = reservoir volume (L)

14.7 = psi/atmosphere.

Quantitative response factors were then calculated for each compound (propane or n-hexane) using the following equation:

$$RF = \frac{\text{area}}{C_s(Vg)}$$

where:

RF = response factor (area/nL-C)

area = peak area for propane or n-hexane

C_s = concentration of propane or n-hexane (ppbv-C (nL-C/L))

Vg = volume of standard used (L).

After analyzing the quantitative standard, the Apple II provided a printout of the calibration data including relative error data as a QC function designed to show the FID variability on a day-to-day basis.

For sample component quantitation, each peak was first identified, then the peak area was calculated according to the response factor for propane or n-hexane (propane for C_2 - C_4 compounds, n-hexane for C_5 - C_{10} compounds). All unidentified peaks were quantitated against n-hexane. The calculation to provide sample component quantitation was:

$$C_s = \frac{\text{area}}{RF\ (Vg)\ (D_f)}$$

where:

C_s = concentration of sample component (ppbv-C)

area = area of sample component peak

RF = daily response factor for propane or n-hexane

Vg = volume of sample analyzed (L)

D_f = dilution factor.

Calculation of the dilution factor for canister samples was discussed in Section 3. Experimentally determined dilution factors and pressure input terms were not used to perform calculations for sorbent and water samples. For sorbent cartridges, the sample volume was calculated from field data. In this case, the amount of desorption gas passed through the cryogenic traps was not used for calculation of sample component concentrations. Instead, the P_2 and P_1 terms were calculated by the operator to correspond to the amount of ambient sample pulled through the trap and the resulting reservoir volume used by the Apple II. This calculation was performed as follows:

$$P_2 - P_1 = \frac{V_s\ (14.7\ \text{psi})}{3.4\ \text{L}}$$

where:

$P_2 - P_1$ = reservoir pressures used for sorbent calculations

V_s = volume of sample pulled through the sorbent

3.4 L = reservoir volume used in Apple II calculation.

For quantitative evaluation of water samples, the calculations required were more complicated since water concentrations must be expressed in mass units. For water sample components, concentrations were calculated based on the weight of carbon of the component per unit volume of water (ng-C/mL). This allowed use of the same calculation method used by the Apple II for gas samples, using the dilution factor term to convert units even though the analytical system was calibrated on a volume carbon basis (RF = area/nL-C). The $P_2 - P_1$ term for water samples was defined as the volume (mL) of sample which was purged. The conversion factor was calculated as follows:

$$D_w = \left(\frac{24.45\ \text{L/M}}{12\ \text{g/M}}\right)\left(\frac{14.7\ \text{psi}}{3.4\ \text{L}}\right)$$

where:

24.45 L/M = the volume of gas occupied by one mole at 25°C

12 g/M = molecular weight of carbon (converts moles to mass of C)

$\frac{14.7\ \text{psi}}{3.4\ \text{L}}$ = conversion of sample volume from liters of gas to mL of liquid entered as $P_2 - P_1$.

The Apple II report provided the name, concentration, retention time, relative retention time, retention time error data, and the TNR value for each compound. The Apple II also provided a total nonmethane hydrocarbon content (TNMHC) value and the percentage of hydrocarbon content which was identified. This was calculated using the following equation:

$$\%\ Id = \Sigma Ic/(\Sigma Ic + \Sigma Uc)\ (100\%)$$

where:

% Id = percentage of nonmethane hydrocarbon identified

ΣIc = sum of identified component concentrations

ΣUc = sum of unidentified component concentrations.

The quantity (ΣIc + ΣUc) is the TNMHC for each sample.

The volume of gas sample which was analyzed and the Julian date of the analyses were also listed at the bottom of the Apple II report.

GC/MS ANALYSIS OF WATER SAMPLES

Water samples collected from each site were also analyzed by gas chromatography/mass spectrometry (GC/MS) to confirm the major VOC species identifications obtained from the GC/PID/FID method and to identify some species which could not be identified by the GC/PID/FID method. The same method of purging the water sample, passing the carrier gas through a Perma Pure drier, and cryogenically concentrating VOC species used for the GC methods, was also used for GC/MS. This technique was described in the previous section. Analyses of water samples by GC/MS were performed using capillary chromatography in the total ion mode (TIM). Conditions used for GC/MS analyses are presented in Table 4-4. Identification of sample components was achieved by computer assisted library searches and manual spectral interpretation.

TABLE 4-4. GC/MS CONDITIONS FOR VOLATILE SPECIES

Instrument	Finnigan 4023
Ionization Voltage	70 eV
Scan Rate	1 amu/sec
Scan Range	35-300 amu
Column	50-meter DB-5 Bonded Fused Silica Capillary
Initial Temperature	-20°C for 2 minutes
Temperature Program	-20°C - 60°C at 30°/min; 60°C - 250°C at 4°/min
Interface	Direct Source Coupled

Since GC/MS is not as sensitive as the GC/PID/FID technique, it was only possible to apply this technique to the more concentrated water samples, and not to the air samples. However, results obtained using the GC/PID/FID technique demonstrated many of the same compounds in both the air and water samples, even though some of the compounds could not be identified by GC since they were not in the initial peak table.

SECTION 5

SITE DESCRIPTIONS AND EXPERIMENTAL MATRICES

Two waste disposal processes were chosen for on-site testing. Criteria for choosing the processes are discussed in Section 1 and a previous document (4). In this section, a description of each site is presented. The proposed sampling matrix for each site is also presented, along with the actual sampling matrix, and discussions of deviations from the proposed matrix.

The quality control limits for proper meteorological conditions for sampling are discussed in Section 3. All sampling was performed under the proper meteorological conditions. Meteorological data pertaining to the quality control limits for sampling are discussed in Section 8. A discussion of meteorological conditions relating to VOC emissions is presented in Section 7.

SITE DESCRIPTION: SITE FB

A diagram of the wastewater treatment facility at Site FB is shown in Figure 5-1. Only the limited air basin was involved in the sampling effort. Wastewater was received from several streams into the equalization basin, where the streams were combined to form a consistent influent to the treatment system. Wastewater from the equalization basin flowed into the limited air basin, which is 16 acres in area, with a depth of 12 feet. Fourteen 75 hp floating surface aerators, arranged in 2 rows, provided 2.5 lb O_2/hp-hr each. Detention time within the basin was estimated at 5 days. Additional aeration basins were used to provide greater detention times.

All profile air sampling was performed near the inlet end of the limited air basin. Water samples were collected from the inlet and outlet of the basin and several intermediate points along the sides. A detailed drawing of the pond, the sites where samples were collected, and wind direction during sampling is presented in Figure 5-2. The rationale for collecting samples in these locations included:

- greater height-to-berm ratios;
- possibly greater flux rates near the influent end of the pond; and
- boat handling with wind considerations.

One of the profile sampling tests was performed directly downwind (∿75 ft) of an aerator. The other two tests were performed between the rows of aerators, with the wind direction in line with the aerator rows. During the profile testing, water samples were collected at each profile sampling site and the inlet and outlet end of the aeration pond. Additional water samples were

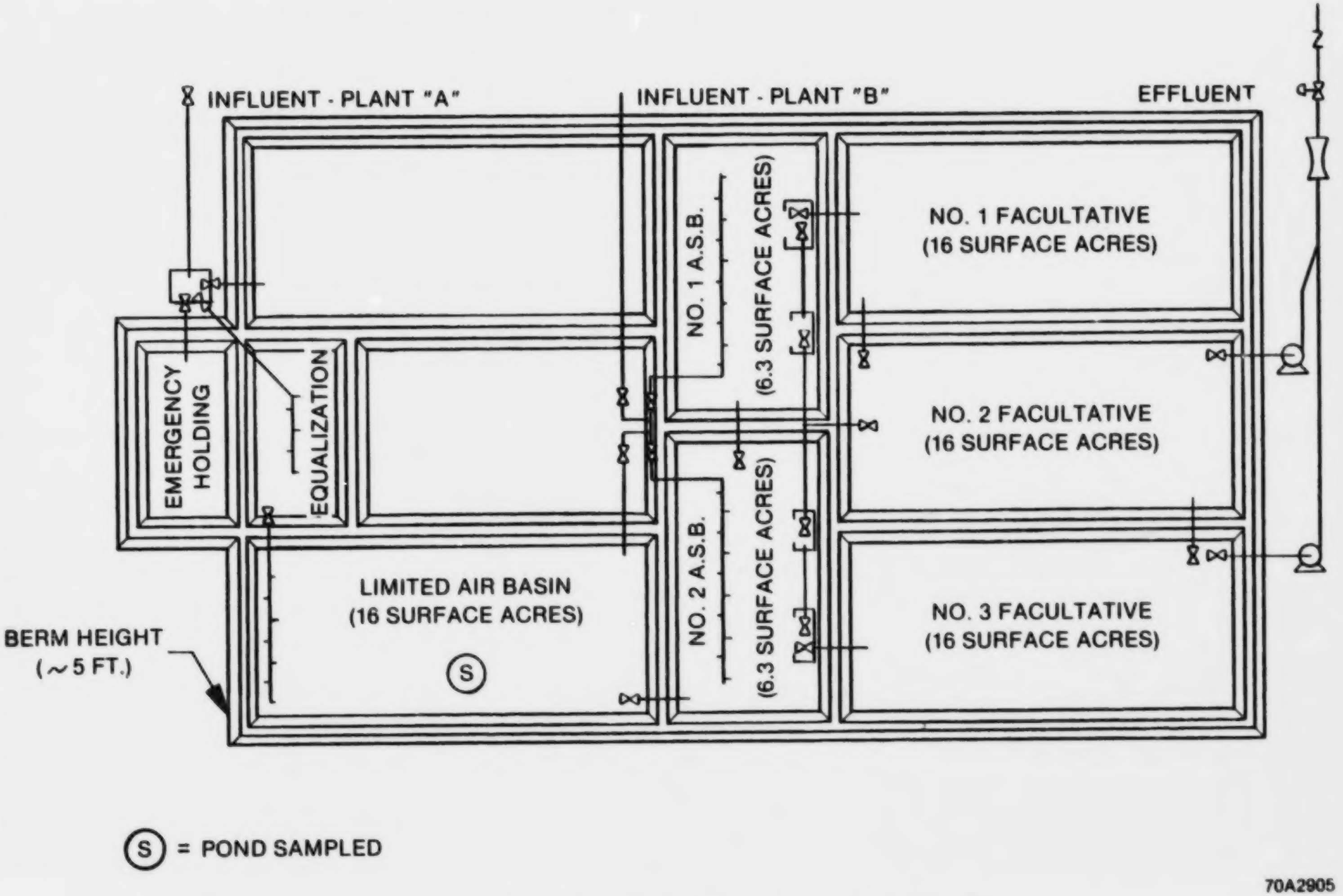

INFLUENT - PLANT "A"
INFLUENT - PLANT "B"
EFFLUENT
NO. 1 A.S.B.
(6.3 SURFACE ACRES)
NO. 2 A.S.B.
(6.3 SURFACE ACRES)
NO. 1 FACULTATIVE
(16 SURFACE ACRES)
NO. 2 FACULTATIVE
(16 SURFACE ACRES)
NO. 3 FACULTATIVE
(16 SURFACE ACRES)
EMERGENCY HOLDING
EQUALIZATION
LIMITED AIR BASIN
(16 SURFACE ACRES)
S
BERM HEIGHT
(~5 FT.)
S = POND SAMPLED
70A2905

Figure 5-1. Diagram of waste ponds for site FB.

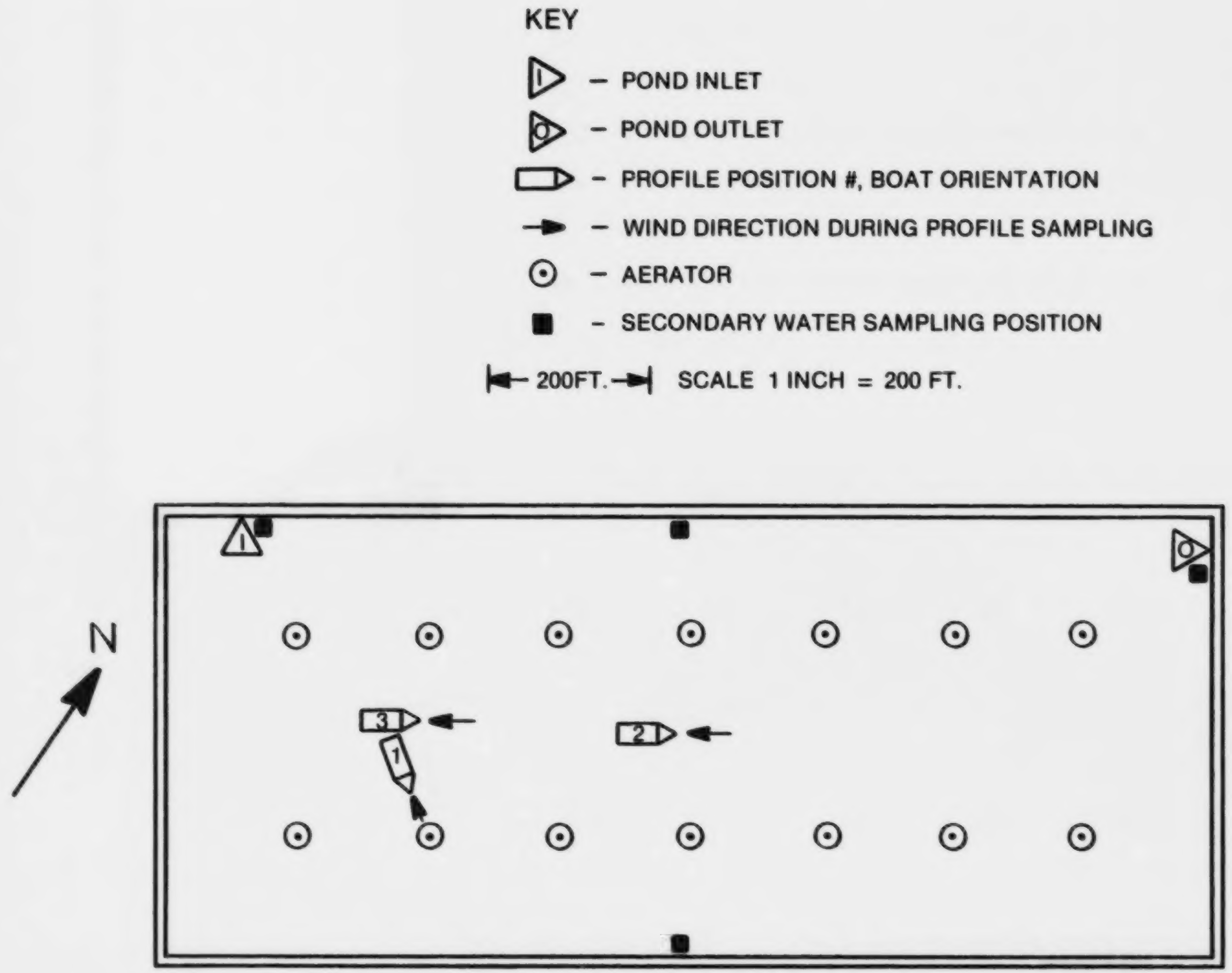

KEY
– POND INLET
– POND OUTLET
– PROFILE POSITION #, BOAT ORIENTATION
– WIND DIRECTION DURING PROFILE SAMPLING
– AERATOR
– SECONDARY WATER SAMPLING POSITION
200FT.
SCALE 1 INCH = 200 FT.
N
I
O
1
2
3

Figure 5-2. Detailed description of sampling at site FB.

70A2906

collected on a later date. The sampling positions for the additional samples are also shown in Figure 5-2.

EXPERIMENTAL SAMPLING MATRIX: SITE FB

The experimental sampling matrix for site FB is presented in Table 5-1. This table includes all tests which were initially proposed (6), and those which were performed. The discrepancies between the proposed on-site tests and those which were performed are:

- The averaging time used for meteorological measurements was 120 seconds instead of 100 seconds. This provided 180 test data points for each measurement type, instead of the proposed 216.
- A manual humidity measurement was used instead of the automatic method initially proposed, changing the number of data points for this procedure.
- Only one cartridge sample and two canister duplicates were collected. The frequency of these quality control procedures was reversed for the second sampling site.
- All scheduled water samples at this site were collected. However, the samples were lost during storage due to an equipment malfunction. Two samples from the primary equilibration pond and four from the secondary limited air basin pond were collected on a later date.

SITE DESCRIPTION: SITE TB

A diagram of the wastewater treatment facility at site TB is shown in Figure 5-3. Plant wastewater first entered a settling pond through a series of three additional small settling ponds for further removal of solids. The main treatment pond was a 28 acre anaerobic facility. This pond was approximately 5 feet deep with 3-foot high berms.

All profile air sampling was performed near the outlet end of the final stage anaerobic pond. Although the height-to-berm ratio was satisfied, this was not ideal since VOC emissions near this end of the pond would be expected to be lower than those near the inlet end. Due to the high winds which were encountered, the boat was maneuvered by ropes from the dike at the outlet end of the pond.

During the profile sampling, water samples were collected at each of the profile sites, and at the pond inlet and outlet. Additional water samples were collected on a later date. Sampling positions are shown in Figure 5-4.

EXPERIMENTAL SAMPLING MATRIX: SITE TB

This experimental sampling matrix for site TB is presented in Table 5-2. This table includes all tests which were initially proposed (6), and those

TABLE 5-1. SAMPLING MATRIX FOR SITE FB

Test	# Heights Performed at	Duration (min)	Total Tests Per Set	Number Of Sets	Total Tests Proposed	Total Tests Performed
PRESAMPLING						
Air Temperature	6	20	72[a]	3[b]	216	180
Wind Speed	6	20	72[a]	3	216	180
Wind Direction	1	20	12[a]	3	36	36
Humidity	1	20	12[a]	3	36	3
SAMPLING						
Air Temperature	6	20	72[a]	3	216	180
Wind Speed	6	20	72[a]	3	216	180
Wind Direction	1	20	12[a]	3	36	36
Humidity	1	20	12	3	36	3
Water Temperature	1	20	3	3	9	9
Inlet Water Sample	1	1	1	1	1	1[e]
Outlet Water Sample	1	1	1	1	1	1[e]
Pond Water Sample	1	1	1	3	3	3[e]
Air Sample	6	20	6	3	18	17
Upwind Air Sample	1	20	1	3	3	3
Duplicate Air Sample	1	20	1	1	1	2[c]
Cartridge Sample	1	20	1	2	2	1
System & Canister Blank	1	20	1	3	3	3
UHP N_2 Blank	0[d]	-	1	1	1	1
Cartridge Blank	1	-	1	1	1	1
Primary Pond Samples	1	1	-	-	-	2
Total					1051	842

[a] Data collected every 1 second and averaged to 100-second intervals.
[b] Three sets performed, each at a different site on the pond.
[c] To be analyzed in duplicate.
[d] One UHP N_2 blank performed for each tank used. These were performed prior to field sampling.
[e] Samples collected but not analyzed (see text).

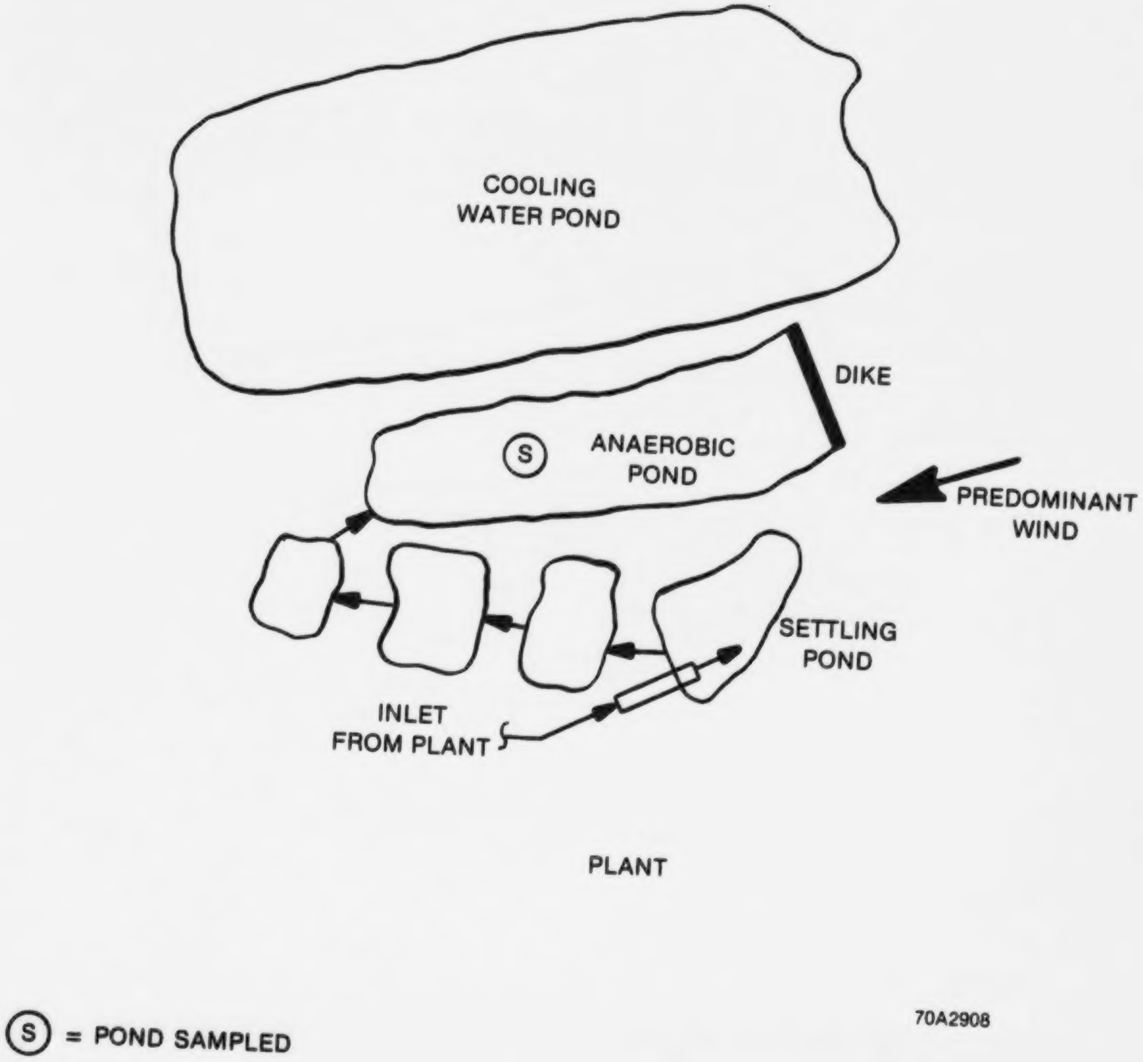
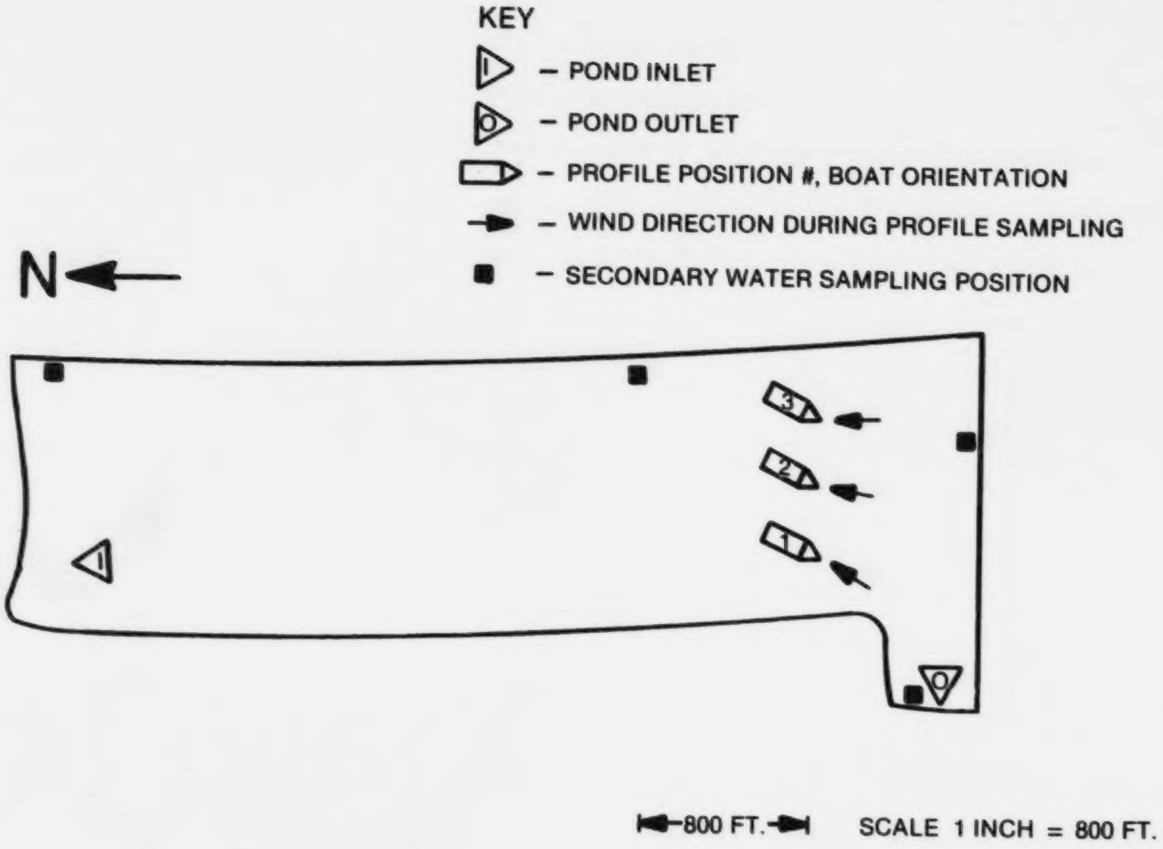

COOLING
WATER POND
DIKE
S
ANAEROBIC
POND
PREDOMINANT
WIND
SETTLING
POND
INLET
FROM PLANT
PLANT
70A2908
S = POND SAMPLED

Figure 5-3. Diagram of waste ponds for site TB.


KEY
I – POND INLET
O – POND OUTLET
– PROFILE POSITION #, BOAT ORIENTATION
– WIND DIRECTION DURING PROFILE SAMPLING
– SECONDARY WATER SAMPLING POSITION
N
I
1
2
3
O
800 FT.
SCALE 1 INCH = 800 FT.

70A2907

Figure 5-4. Detailed description of sampling at site TB.

TABLE 5-2. SAMPLING MATRIX FOR SITE TB

Test	# Heights Performed at	Duration (min)	Total Tests Per Set	Number Of Sets	Total Tests Proposed	Total Tests Performed
PRESAMPLING						
Air Temperature	6	20	72[a]	3[b]	216	216
Wind Speed	6	20	72[a]	3	216	216
Wind Direction	1	20	12[a]	3	36	36
Humidity	1	20	12[a]	3	36	3
SAMPLING						
Air Temperature	6	20	72[a]	3	216	216
Wind Speed	6	20	72[a]	3	216	216
Wind Direction	1	20	12[a]	3	36	36
Humidity	1	20	12	3	36	3
Water Temperature	1	20	3	3	9	9
Inlet Water Sample	1	1	1	1	1	1
Outlet Water Sample	1	1	1	1	1	1
Pond Water Sample	1	1	1	3	3	3[e]
Air Sample	6	20	6	3	18	18
Upwind Air Sample	1	20	1	3	3	4
Duplicate Air Sample	1	20	1	2	2	1[c]
Cartridge Sample	1	20	1	1	1	2
System & Canister Blank	1	20	1	3	3	3
UHP N_2 Blank	0[d]	-	1	1	1	1
Cartridge Blank	1	-	1	1	1	1
Primary Pond Samples	1	-	-	-	-	2
Total					1051	988

---

[a] Data collected every 1 second and averaged to 100-second intervals.

[b] Three sets performed, each at a different site on the pond.

[c] To be analyzed in duplicate

[d] One UHP N_2 blank perfomred for each tank used. These were performed prior to field sampling.

[e] Samples collected but not analyzed (see text).

which were performed. The discrepancies between the proposed on-site tests and those which were performed are:

- A manual humidity measurement was used instead of the automatic method initially proposed, changing the number of data points for this procedure.
- All scheduled water samples were collected. However, all but two were lost during storage due to an equipment malfunction. Four samples from the main pond were collected on a later date.

ANALYTICAL MATRIX: SITES FB AND TB

The analytical matrix for samples collected from both sites is presented in Table 5-3. This table includes all analyses which were initially proposed (6), and those which were actually performed. The discrepancies between the proposed analyses and those which were performed are:

- Of the 10 water samples originally collected, 8 were lost during storage due to an equipment malfunction. PT/GC/MS and PT/GC/FID/PID analyses were performed on the remaining samples.
- Twelve additional water samples were collected and analyzed by PT/GC/FID/PID. Three of these were also analyzed by PT/GC/MS.
- One mast sample was lost during collection and one set of nested analyses was not performed because the 1.0 L EPA canisters did not contain sufficient sample for duplicate analysis.
- One additional upwind sample was collected.
- A number of quality assurance audit samples were analyzed to help determine system performance. These were not initially scheduled.

TABLE 5-3. SUMMARY OF SAMPLES TO BE COLLECTED AND ANALYZED

Samples Type	# From Site TB	# From Site FB	Total Scheduled Samples	Analysis	Total Scheduled Analyses	Total Performed
Water	5	5	10	PT/GC[a]	10	2
				PT/GC/MS[b]	2	2
Water - Primary Pond	2	2	4	PT/GC	0	4
				PT/GC/MS	0	1
Air Mast Samples	20	19	39	CC/GC[c]	45	42
Upwind Air Samples	3	3	6	CC/GC	6	7
Cartridge Samples	1	2	3	TD/GC[d]	3	3
System Blanks	3	3	6	CC/GC	6	6
Cartridge Blanks	1	1	2	TD/GC	2	2
UHP N_2 Blank	-	-	-	CC/GC	1/tank	1
QA Audit Samples	4	-	-	CC/GC	0	-
	—	—	—		—	—
TOTAL	37	33	66	75	75	70

[a] Purge and trap with gas chromatographic PID/FID analysis.
[b] Purge and trap with gas chromatographic mass spectrometry analysis.
[c] Cryogenic concentration with gas chromatographic PD/FID analysis.
[d] Thermal desorption with gas chromtographic PID/FID analysis.

SECTION 6

DATA REDUCTION AND PROCESSING

All meteorological and chemical data were placed in a computer file to provide ready access for flux calculations and statistical data analyses. In this section, the procedures used for computer processing of data are discussed. In addition, procedures for the evaluation of flux rates and establishment of confidence limits using the Concentration-Profile (C-P) technique and the methods and data used for the predictive model calculations are described.

DATA TRANSCRIPTION

Processed chromatographic and meteorological data were transcribed onto preformatted data collection forms. The data collection forms were then keypunched, verified, and input into a data base which used the Statistical Analysis System (SAS), a computer system for data and statistical analysis. Data summary reports were output from the data base and manually checked for errors. After corrections were made, sample data reports and run summaries were prepared. All chemical species were given a code number and a chemical classification. For each sample, compounds within chemical classes were summed to provide total organic class concentrations in air and water, and a total nonmethane hydrocarbon content (TNMHC). The chemical classes which were considered were: alkanes, alkenes, aromatics, oxygenated hydrocarbons (includes aldehydes, ketones, and alcohols), chlorinated saturated hydrocarbons and chlorinated unsaturated hydrocarbons.

MEASURED CHEMICAL FLUX CALCULATIONS

This section presents the working equations for the C-P technique. A complete development of the theory can be found in Reference 1.

The C-P technique estimates chemical flux rates based on experimental measurements of wind velocity and temperature profiles in the boundary layer over wastewater ponds. Six VOC concentrations of each meteorological variable, along with ambient VOC concentration data distributed in a logarithmic vertical profile from the water surface, were taken at three different locations on the pond site. Based on these measurements, the equation used to determine the vertical flux of the chemical (i.e., species i) from the water surface is given as:

$$E_i = -(D_i/D_{H_2O})^{2/3} \; S_v \; S_i \; K^2/\phi_m^2 \; S_c \qquad (6\text{-}1)$$

where:

E_i = estimate of the flux rate of organic species i ($ng\text{-}C/cm^2\text{-}sec$)

D_i = molecular diffusivity of organic species i in air (ft^2/hr)

D_{H_2O} = molecular diffusivity of water vapor in air (1.05 ft^2/hr)

S_v = slope of the best linear fit through the linear portion of the data of wind velocity (cm/sec) vs. ln y, where y is the sample height (cm) above the water surface

S_i = slope of the best linear fit through the linear portion of the data of chemical concentration ($ng\text{-}C/cm^3$) for organic species i vs. ln y

K = Von Karmon's constant (0.4)

ϕm = Businger wind sheer parameter

S_c = turbulent Schmidt number, expressed as a function of the Richardson number. The Richardson number (R) is related to atmospheric stability and is computed from temperatures and wind velocities in the boundary layer by:

$$R = \frac{g}{T}\left(\frac{b_1}{b_2{}^2}\right) \qquad (6\text{-}2)$$

where:

R = Richardson number, a negative value of R results if the air is unstable, if R = 0, the air is neutral and if R >0, the air is stable (dimensionless)

g = gravitational acceleration constant (980.7 cm/sec^2)

T = average temperature (K)

b_1 = slope of the best linear fit through the linear portion of the data of temperature (K) vs. sensor height (cm) above the water surface

b_2 = slope of the best linear fit through the linear portion of the data of wind speed (cm/sec) vs. sensor height (cm) above the water surface

The Richardson number provides a means of assessing the low wind speed limitation of Equation 6-1 for flux determination and application of the stability correction factor $(\phi_m^2 \; S_c)^{-1}$. If conditions are stable, Equation 6-1 should be used only for $|R| \leq 1.0$. If conditions are unstable, Equation 6-1 should be used for $|R| \leq 4.0$. The correction factor is then estimated by:

$$(\phi_m S_c)^{-1} = (1 \pm 50 R)^{\pm 1/2} \qquad (6\text{-}3)$$

where -50 and +1/2 apply for unstable conditions and +50 and -1/2 apply for stable conditions. The correction factor is unity for neutral conditions.

Equation 6-3 is an empirical correlation that corrects the neutral condition, concentration profile flux estimate for water vapor (i.e., $E_{H_2O} = -S_{H_2O} S_v K^2$) to the actual water vapor flux from ground sources under non-neutral conditions. This water vapor flux calibration factor and associated $|R|$ values place limitations on the use of Equation 6-1 for flux estimates since it has not been verified outside the given R range. The 2/3 power ratio of the molecular diffusivities of the chemical of interest to that of water vapor (i.e., $\{D_i/D_{H_2O}\}^{2/3}$) corrects the equation for the chemical for which the flux is desired. Both the correction factor and the diffusivity ratio are dimensionless.

The three equations presented above are the working formulas of the C-P technique. The following sections discuss the data manipulations and a sample calculation of the flux rate illustrating their use.

Data Conversion Factors

Analytical and field measurement data were collected using a variety of units. The types of measurements which were made and the units for these are discussed in Sections 3 and 4. To apply these data to flux calculations a number of conversions were required. These conversion factors are discussed below.

Temperature--

Water and air temperatures were measured in degrees Fahrenheit (°F). These temperatures were converted to degrees Kelvin (K) for the flux calculation using:

$$K = (°F - 32°)\ 5/9 + 273°$$

Wind Speed--

Wind speed was measured in miles per hour (mph) and converted to centimeters per second (cm/sec) using:

$$\text{cm/sec} = \text{mph} \times 44.7$$

Sensor Height--

Sensor heights were measured in inches (in) and converted to centimeters (cm) using:

$$\text{cm} = \text{in} \times 2.54$$

Chemical Concentrations in Air--

Chemical concentrations were measured as parts per billion of carbon by volume (ppbv-C) in dry air. For the flux calculation, concentrations in mass per unit volume of wet air (humidity when the sample was collected) were required. The conversion required two steps, converting from volume of carbon in the gas phase to mass of carbon in the gas phase, and converting from dry to wet volume. The volume to mass calculation can be accomplished as follows:

$$\text{ng-C} = \frac{\text{nL-C} \times 12 \text{ ng/nmole}}{22.4 \text{ L/nmole} \times \frac{T_a}{273}} \qquad (6\text{-}4)$$

where T_a is the average air temperature from the lowest to highest sample arm. Theoretically, the temperature of each arm should be used for each corresponding air sample. However, differences in temperatures at the individual heights were insignificant with respect to the average temperatures.

Volume correction data for all sampling runs at the two sites are presented in Table 6-1. These data were used to calculate the actual sample volume including the volume of moisture removed from the sample prior to volume measurement. When combining all conversion factors using meteorological data collected for each run, the variation between runs and sites was only 0.4%. Therefore, one conversion factor was used for all air data. The final conversion factor including conversion from liters (L) of sample to cubic centimeters (cm^3) was:

$$\text{ng-C/cm}^3 \text{ (wet)} = \text{ppbv-C (dry)} \times 4.815 \times 10^{-4}$$

Sample Calculation

The data collected at site FB (sample 1), presented in Table 6-2, were used to solve for the vertical flux rate of benzene.

Using Equations 6-1 through 6-3, the solution was as follows:

$$(D_{\text{Benzene}}/D_{H_2O})^{2/3} = \left(\frac{0.370}{1.05}\right)^{2/3} = 0.499$$

$$S_{\text{Benzene}} = -0.00543 \text{ ng-C/cm}^3$$

$$S_v = 72.958 \text{ cm/sec}$$

For the Richardson number,

$g = 980.7 \text{ cm/sec}^2$

$T = 297.422$ K

TABLE 6-1. METEOROLOGICAL DATA USED FOR CHEMICAL CONCENTRATION CORRECTIONS

Parameter	SITE FB			SITE TB		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Ave. Mast Temp. °C	24.8	22.2	22.0	23.3	23.8	25.2
Volume to Mass Conversion	0.4911	0.4954	0.4958	0.4936	0.4928	0.4904
Relative Humidity (%)	73	86	91	88	81	77
Water Vapor Pressure (mm Hg)	17.14	17.26	18.04	18.87	17.91	18.51
Barometric Pressure (mm Hg)	758.0	758.0	758.0	758.3	758.3	758.3
Water Volume Correction*	1.0231	1.0233	1.0244	1.0255	1.0242	1.0250
Total Conversion Factor	0.4800	0.4841	0.4840	0.4813	0.4811	0.4785

Ave. Conversion Factor ±SD (%CV) 0.4815 ± 0.0022 (0.4%)

*Water volume correction = barometric pressure/barometric pressure-water vapor pressure.

TABLE 6-2. DATA USED FOR SAMPLE FLUX CALCULATION

Sampling Position	Wind Speed (cm/sec)			Temperature (K)		Benzene Concentration (ng-C/L)		
	Avg.	Ht.*	Ln(Ht)	Avg.	Ht.	Avg.	Ht.	Ln(Ht)
1	268.2	36.8	3.6055	298.17	27.9	-	7.6	2.0282
2	-	69.9	4.2471	297.72	61	.02392	33	3.4965
3	357.6	107	4.6728	297.39	98	.016612	68.6	4.2283
4	402.3	166	5.1120	297.33	157	.023979	127	4.8442
5	402.3	258	5.5530	-	249	.017286	220	5.3936
6	447.0	398	5.9865	296.50	389	.006789	360	5.8861

* Ht. = height above pond surface (cm)

$b_1 = -0.00408$ K/cm

$b_2 = 0.43131$ cm/sec

then:

$$R = \frac{(980.7 \text{ cm/sec}^2)\ (-0.00408 \text{ K/cm})}{(297.422 \text{ K})\ (0.43131 \text{ cm/sec})^2} = -0.0723$$

$$[\phi_m^2\ S_c]^{-1} = [1 - 50\ (-0.0723)]^{1/2} = 2.1483$$

The flux rate for benzene was computed as:

$$E_{Benzene} = -(D_{Benzene}/D_{H_2O})^{2/3}\ S_v\ S_i\ K^2/\phi_m^2\ S_c$$

$$= -(0.499)\ (72.958 \text{ cm/sec})\ (-0.00543 \text{ ng/cm}^3)\ (0.4)^2\ (2.1483)$$

$$= 0.00679 \text{ ng/cm}^2\text{-sec}$$

which is the flux rate for benzene given in Section 7 for site FB-1.

MODEL PREDICTIONS

Flux rates were predicted by applying a model developed by Thibodeaux, et al. (1), which was described in a recent article by Hwang (2). This model requires that the water temperature and aqueous concentrations of the compounds of interest be known. The model also uses input data pertaining to atmospheric conditions and impoundment characteristics. The procedures used in applying the predictive model are described in this section. The nomenclature and definitions of equation terms used in this section are shown in Table 6-3. The units in this table are mixed. This is due to the fact that many of the empirical relationships were developed using English and/or mixed units. They are consistent with Reference 2. In cases where inconsistencies were found between References 1 and 2, Reference 1 was consulted.

The emission rate (Q_i) of a compound from water can be expressed by:

$$Q_i = K_L \cdot A(x_i - x_i^*)MW_i \qquad (6\text{-}5)$$

The area of the impoundment (A) and the molecular weight of the compound (MW_i) are known, and the overall mass transfer coefficient (K_L) can be calculated from:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{K \cdot k_g} \qquad (6\text{-}6)$$

In Equation 6-6, k_L and k_g are the liquid and gas-phase mass transfer coefficients, respectively, and K is the vapor-liquid equilibrium constant. Since the concentration of the compound in the air (x_i^*) can generally be assumed to be negligible compared to the liquid phase concentration (x_i), Equation 6-5 becomes:

TABLE 6-3. NOMENCLATURE FOR FLUX RATE MODEL*

A = surface are of disposal facility, cm^2

a_v = surface area per unit volume of surface impoundment, ft^{-1}

C_i^* = concentration of component i in the air space in the immediate vicinity of the waste (or in equilibrium with the waste), g/cm^3

D = diffusion coefficient, cm^2/sec (note: $D_{i \cdot H_2O}$ is the diffusion coefficient of component i in water).

D_{wi} = diffusivity of component i in the waste, cm^2/sec

d = diameter of aerator turbine or impeller, cm

d_e = effective diameter of quiescent area of surface impoundment, m

g = gravitational or conversion constant, ft/sec^2

H = Henry's law constant, $atm/mol/m^3$

H_c = Henry's law constant in concentration ($C_{ij} = H_c C_{iL}$)

H_o = effective depth of surface impoundment, ft

J = oxygen-transfer rating of surface aerator, normally about 3 $lb\text{-}O_2/hr\text{-}hp$

K = vapor-liquid equilibrium constant

(Continued)

TABLE 6-3. (Continued)

K_L = overall mass-transfer coefficient, g-mol/ $cm^2 \cdot sec$

k_g, k_L = gas and liquid-phase mass-transfer coefficients, respectively, g-mol/$cm^2 \cdot sec$

$k_{g.i}$ = gas-phase mass-transfer coefficient of component i in air, g-mol/$cm^2 \cdot sec$

MW_i = molecular weight of component i, g/g-mole

N_{FR} = Froude number, $d\ \omega^2/g$

N_P = power number, $P_r g/\rho_L d^5 \omega^3$

N_{Re} = gas Reynolds number, $\rho_g d^2 \omega/\mu_g$

N_{sc} = gas Schmidt number, $\mu_g/\rho_g D_{i,\ air}$

P = total pressure, mm Hg

P° = pure component vapor pressure, mm Hg

POWR = total power input to aerators in aerated surface impoundment, Hp

P_r = power to impeller, ft-lb force/sec

Q = rate of emissions from a disposal facility, g/sec

q = emission rate per unit area of area source, g/$cm^2 \cdot$ sec

(Continued)

TABLE 6-3. (Continued)

R = gas constant, cm^3· mm Hg/K · mol

Re* = roughness Reynolds number

r = recycle ratio, volume flow-rate of recycle/volume flow rate of feed

S = substrate concentration, ug/liter

T = temperature, K

U_o = surface velocity, ft/sec. Normally 0.035 x wind speed for natural surface

U_{air} = wind speed, m/hr

U_{10} = wind speed, cm/s**

V = volume of surface impoundment in region of effect of aerators, ft^3

x = liquid-phase mole fraction

y = gas-phase mole fraction

Z_{10} = height where U_{10} measured, cm**

(Continued)

TABLE 6-3. (Continued)

GREEK LETTERS

α = oxygen transfer correction factor

μ = viscosity, g/cm • sec

θ = temperature, °C

γ = activity coefficient

ρ = density, lb/ft^3

ω = rotational speed of turbine impeller, rad/sec

ν = kinematic viscosity, cm^2/sec**

SUBSCRIPTS

air = air

c = convective

H_2O = water

g = gas

i = hazardous component i

j = hazardous component j

L = liquid

(Continued)

TABLE 6-3. (Continued)

O_2 = oxygen

T = turbulent

Tol = toluene

w = waste

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*After Ref. 2.

**Not included in Ref. 2.

$$Q_i = K_L \cdot A \cdot x_i \cdot MW_i \qquad (6\text{-}7)$$

Since x_i was available from the analyses of liquid-phase samples obtained at each site, the only variable needed to solve Equation 6-7 is K_L. For impoundments with aerators, K_L must be calculated for the turbulent and convective regions. Then an area-average overall mass-transfer coefficient is calculated from:

$$K_L = (K_L)_c \frac{A_c}{A} + (K_L)_T \frac{A_T}{A} \qquad (6\text{-}8)$$

There are a number of simplifying assumptions that are inherent in the development of this model. Some have been mentioned already. Other major assumptions include:

- The system is at steady state. Thus, no provisions are included for the effects of changing compositions, reactions, or biological degradation.
- The impoundment behaves as an ideal solution. This assumption implies that there are no interferences or interactions between species in the aqueous phase.
- The impoundment surface can be effectively divided between turbulent (aerated) surfaces and normal (unaerated) surfaces.
- The four individual mass transfer coefficients, obtained from empirical relationships, apply within the desired accuracy to this system.

Liquid-Phase Convective Regions

For the convective (non-aerated) regions, the liquid-phase mass-transfer coefficients ($(k_L)_c$, cm/hr) were calculated from Reference 12:

$$(k_L)_c = [11.4(Re^*)^{0.195} - 5] \frac{D_{i \cdot H_2O}}{D_{Tol \cdot H_2O}} \qquad (6\text{-}9)$$

Re*, the roughness Reynolds number, was calculated from Reference 12:

$$Re^* = \frac{7.07 \times 10^{-3})(Z_{10})(U_{10})^{1.25}}{(\nu_{air}) \exp(56.6/U_{10}^{0.25})} \qquad (6\text{-}10)$$

At 25°C, $\nu_{air} = 0.15$ cm^2/sec. Although U_{10} should be measured at 10 meters above the water surface, the wind speeds available at sites FB and TB were measured at 4 meters. Therefore, Z_{10} equaled 400 cm.

For site FB: $U_{10} = 492$ cm/sec and $Re^* = 0.263$

For site TB: $U_{10} = 894$ cm/sec and $Re^* = 2.95$

In Equation 6-9, the ratio of diffusion coefficients (D_i/D_j) can be approximated by Reference 2:

$$\frac{D_i}{D_j} = \left(\frac{MW_j}{MW_i}\right)^{0.5} \qquad (6\text{-}11)$$

Toluene is the reference compound (j) and therefore Equation 6-9 becomes:

For site FB: $(k_L)_c = \frac{36.3}{(MW_i)^{0.5}}$

For site TB: $(k_L)_c = \frac{87.1}{(MW_i)^{0.5}}$

The above coefficients, $(k_L)_c$, are in units of cm/hr. In units of lb-mole/ft^{2}hr, the coefficients become:

For site FB: $(k_L)_c = \frac{4.12}{(MW_i)^{0.5}}$

For site TB: $(k_L)_c = \frac{9.87}{(MW_i)^{0.5}}$

Gas-Phase Convective Regions

For the convective regions, the gas-phase mass transfer coefficients ($(k_g)_c$, lb-mole/ft-hr) were calculated from Reference 2:

$$(k_g)_c = 0.0958\, U_{air}^{0.78}\, N_{sc}^{-0.67}\, d_e^{-0.11}\, \frac{\rho_{air}}{MW_{air}} \qquad (6\text{-}12)$$

At 25°C, $\rho_{air} = 0.075$ lb/ft^3 and $MW_{air} = 29$ lb/lb mole.

For site FB: $U_{air} = 17700$ meter/hr

For site TB: $U_{air} = 32200$ meter/hr

For site FB, the effective diameter was calculated by first subtracting the turbulent area from the total area of the impoundment. Turbulent areas were estimated using data from Reference 1. Site FB had 14 aerators with 76 hp, 900 rpm, and 52 cm blades. The closest match of parameters from Reference 1 was for 75 hp, 1200 rpm, and 60 cm blade aerators, which corresponds to a turbulent area of 1452 ft^2. Therefore, the site FB convective area (A_c) and effective diameter (d_e) are:

$$A_c = 16 \text{ acres} - (14)\,(1452 \text{ ft}^2) = 15.53 \text{ acres} = 62860 \text{ m}^2$$

$$d_e = \left(\frac{4A_c}{\pi}\right)^{0.5} = (283) \text{ m}$$

For site TB: A_c = 28 acres = 113,300 m^2 and d_e = 380 m

The Schmidt number (N_{sc}) was calculated from:

$$N_{sc} = \frac{\mu_g}{\rho_g \, D_{i\ air}} \qquad (6\text{-}13)$$

For air at 25°C, $\frac{\mu_g}{\rho_g} = \nu_{air} = 0.15\ cm^2/sec = 0.58\ ft^2/hr$.

Therefore:

$$N_{sc} = 0.58/D_{i \cdot air}$$

Values of volume diffusivities ($D_{i \cdot air}$) were estimated by correcting measured diffusivity values (12) to the temperatures of interest (25°C) by the following expression:

$$D_{T_2} = (D_{T_1}) \left(\frac{(T_2)^x}{(T_1)^x}\right)\left(\frac{\Omega_1}{\Omega_2}\right) \qquad (6\text{-}14)$$

The temperature exponent (x) was estimated as described in Reference 13, as a function of the reduced temperature of each compound. For the compounds of interest, reduced temperatures are in the range for which x = 2.

The value of Ω is also a function of temperature and can be estimated from the Lennard-Jones Parameters (ε/K). Values of ε/K were taken from Reference 13 and Reference 14. The values of Ω (as a function of KT/ε) were taken from Reference 14.

The properties used in deriving volume diffusivities (D_i) for the compounds of interest at sites FB and TB are shown on Table 6-4 along with the temperature compensated values of $D_{i \cdot air}$.

The above equations yield the following values for $(k_g)_c$:

For site FB:

$$(k_g)_c = (0.0958)(17710)^{0.78}\,(283)^{-0.11}\,\frac{(0.075)}{(29)}\,N_{sc}^{-0.67}$$

$$(k_g)_c = (0.296)N_{sc}^{-0.67} = (0.296)\,\frac{(0.58)^{-0.67}}{D_i^{-0.67}} = (0.394)(D_i)^{0.67}$$

For site TB:

$$(k_g)_c = (0.0958)(32200)^{0.78}\,(380)^{-0.11}\,\frac{(0.075)}{(29)}\,(0.58)^{-0.67}\,(D_i)^{0.67}$$

$$(k_g)_c = (0.609)(D_i)^{0.67}$$

TABLE 6-4. PROPERTIES USED TO ESTIMATE DIFFUSIVITIES

Compound	T_c (K)	T_r	D_{T_1} (ft^2/hr)	T_1 (K)	ε/K (K)	Ω_{T_1}	Ω_{T_2}	D_{T_2} (ft^2/hr)
Benzene	562	0.53	0.298	273	440	1.845	1.764	0.370
Acetone	508	0.59	0.422	273	560	2.097	2.006	0.523
Cyclohexane	553	0.54	0.333	318	324	1.450	1.503	0.281
Diethyl ether	467	0.64	0.301	273	350	1.634	1.562	0.374
Total aromatics[1]	617	0.48	0.255	273	473	1.920	1.830	0.316
Indene[2]	638	0.47	0.186	273	495	1.966	1.877	0.231
Styrene[3]								0.277

[1] Using properties of ethylbenzene

[2] Using properties of propylbenzene

[3] No literature value of D_{T_1}. D_{T_2} estimated by methods from Ref. 13 and 15

T_c = critical temperature from Ref. 13

T_r = reduced temperature = T_2/T_c = $298/T_c$. Note: from T_r = 0.3 to 0.6, $x \simeq 2.0$ from Ref. 13

D_{T_1} = Diffusivity from Ref. 12

ε/K = Lennard Jones Parameter from Ref. 13 and 14

Ω = collision integral from Ref. 14

(K) = degrees Kelvin

Liquid-Phase Turbulent Regions

The liquid-phase mass transfer coefficients ($(k_L)_T$, lb mole/ft^2-hr) for turbulent regions were calculated from:

$$(k_L)_T = \frac{(J)(POWR)(1.024)^{\theta-20}(\alpha)(10^6)}{(a_v)(V)(165.04)}\left(\frac{D_{i\cdot H_2O}}{D_{O_2\cdot H_2O}}\right)^{0.5} \qquad (6\text{-}15)$$

where:

$\theta = 25°C$

$POWR = 75$ hp

$\alpha = 0.825$ (from Ref. 1: α varies from 0.8 to 0.85)

$a_v = 0.0625$ ft^2/ft^3 (from Ref. 1)

$V = 23240$ ft^3 (from Ref. 1)

Substituting Equation 6-11 for $\frac{D_{i\cdot H_2O}}{D_{O_2\cdot H_2O}}$, Equation 6-15 becomes:

$$(k_L)_T = \frac{1.52 \times 10^3}{(MW_i)^{0.25}}$$

Gas-Phase Turbulent Regions

The gas-phase mass-transfer coefficients for turbulent regions ($(k_g)_T$, lb-mole/ft^2-hr) were calculated from Reference 2:

$$(k_g)_T = 0.00039\,\frac{\rho_g D_{i\cdot air}}{d}\,(N_{Re})^{1.42}(N_{FR})^{-0.21}(N_p)^{0.4}(N_{sc})^{0.5} \qquad (6\text{-}16)$$

$D_{i\cdot air}$ was calculated in a previous section. The values shown in Table 6-4 were also used to solve Equation 6-16. At 25°C, $\rho_g = 0.075$ lb/ft^3. Since d is the impeller diameter, d = 22/12 = 1.83 ft. The Reynolds number (N_{Re}) was calculated from:

$$N_{Re} = \frac{(\rho_g)(d)^2(\omega)}{\mu_g} \qquad (6\text{-}17)$$

$$\rho_g/\mu_g = 1/\nu_g = \frac{1}{0.15\ \text{cm}^2/\text{sec}} = \frac{1}{1.16 \times 10^{-4}\ \text{ft}^2/\text{sec}}$$

$d = 1.83$ ft

$\omega = 900$ rpm - 1.57 radians/sec

Therefore:

$$N_{Re} = \frac{(1.83)^2(1.57)}{1.61 \times 10^{-4}} = 3.27 \times 10^4$$

The Froude number (N_{FR}) was calculated from:

$$N_{FR} = \frac{(d)(\omega)^2}{g} \tag{6-18}$$

Therefore, since $g = 32$ ft/sec^2:

$$N_{FR} = \frac{(1.83)(1.57)^2}{32} = 0.141$$

The Power number (N_p) was calculated from:

$$N_p = \frac{(P_r)(g_c)}{(\rho_L)(d)^5(\omega)^3} \tag{6-19}$$

$$P_r = 75 \text{ hp} = 41250 \text{ ft-lb}_f\text{/sec}$$

where:

$$g_c = 32.2 \, \frac{\text{ft-lb}_m}{\text{lb}_f\text{sec}^2}$$

$$\rho_L = 62.2 \text{ lb}_f/\text{ft}^3.$$

Therefore:

$$N_p = \frac{(41250)(32.2)}{(62.2)(1.83)^5(1.57)^3} = 269$$

The Schmidt number (N_{sc}) was calculated above and $N_{sc} = (0.58)/(D_i)$ was used to solve Equation 6-16. Substituting the above values in Equation 6-16:

$$(K_g)_T = \frac{(0.00039)(0.075)(3.27\text{x}10^4)^{1.42}}{1.83} (0.141)^{-0.21} \; (269)^{0.4} \left(\frac{0.58}{D_i}\right)^{0.5} D_i$$

$$= (443)(D_i)^{0.5}$$

To obtain $(k_g)_T$ in lb-mole/ft^2-hr:

$$(k_g)_T = (443)(D_i)^{0.5}/MW_i$$

The above Equations 6-9 through 6-19 were used to calculate mass transfer coefficients for each compound. To calculate the overall mass transfer coefficient (K_L), however, the equilibrium constant (K) is needed for each compound of interest. The equilibrium constant can be estimated using Henry's law constants or Raoult's law. The use of Henry's law constants is most appropriate for those compounds which are sparingly soluble in water. The Henry's law constant has been determined experimentally for some compounds. In cases where experimental values are unavailable, Henry's law constant (H) can be estimated from volatility and solubility data using the following relationship:

$$H_i = \frac{P_i}{S_i} \qquad (6\text{-}20)$$

where:

H_i = Henry's law constant for component i (atm-m^3/mol)

P_i = vapor pressure of pure component i at the system temperature (atm)

S_i = solubility of component i in water (mol/m^3).

The equilibrium constant (K_i) can then be calculated for any component from the following equation:

$$K_i = \frac{H_i \times 10^6}{P\ MW_i} \qquad (6\text{-}21)$$

where:

K_i = equilibrium constant for component i

P = total pressure (atm)

MW_i = molecular weight of component i.

For those compounds which are completely miscible in water, and for which Henry's law constants could not be found, the equilibrium constant can be estimated from Raoult's law:

$$K_i = \frac{P_i}{P} \qquad (6\text{-}22)$$

The values of the Henry's law constants for the compounds of interest in this study are included in Table 6-5. The equilibrium constants are also presented in this table. Henry's law constants were used to calculate the equilibrium constants for all components with the exception of acetone. Acetone is completely miscible with water, and the Henry's law constant (if determined) was not found. Raoult's law was used to estimate the equilibrium constant for acetone.

The overall K values were calculated from Equation 6-6:

$$\frac{1}{K_L} = \frac{1}{k_L} \quad \frac{1}{K \cdot k_g}$$

For site TB, this equation yields the K_L needed for solving Equation 6-5. For site FB, K_L was calculated for the turbulent and convective regions, and then Equation 6-8 was used to calculate K_L:

$$K_L = (K_L)_c \frac{Ac}{A} + (K_L)_T \frac{A_T}{A}$$

At site FB:

$$A_T/A = \frac{0.47 \text{ acres}}{16 \text{ acres}} = 0.0294$$

$$A_c/A = \frac{15.53}{16.} = 0.9706$$

Measured concentrations of compounds (C_i) in the water were expressed as ng-C/mL of water. Therefore, Equation 6-7 can be written as:

$$Q_i = (K_L)(A)(C_i) \frac{18}{(0.997)(10^9)} \qquad (6\text{-}23)$$

where C_i = aqueous concentration in ng/mL and Q_i is expressed in lb/hr. Note: the molecular weight of the compound is divided out of the equation and:

$$Q_i = K_L A C_i (1.81 \times 10^{-8})$$

For site FB: $A = 16 \text{ acres} = 6.97 \times 10^5 \text{ ft}^2$

For site TB: $A = 28 \text{ acres} = 1.22 \times 10^6 \text{ ft}^2$

The units of flux are expressed as ng/cm^2-sec.

TABLE 6-5. HENRY'S LAW CONSTANTS AND EQUILIBRIUM CONSTANTS

Compound	Vapor Pressure @ 25°C, atm	Solubility in Water @ 25°C, mol/m^3	Henry's Law Constants, atm-m^3/mol	Equilibrium Constant, K_i[d]
Benzene	0.125	22.8	5.28×10^{-3}	304
Acetone	0.250	00	—[b]	0.250
Cyclohexane	0.132	0.117	1.12	6.22×10^{4}
Diethyl Ether	0.524	1010	0.51×10^{-3}	28.3
Total Aromatics[a]	0.013	1.95	6.75×10^{-3}	3.58×10^{2}
Indene	0.0029	0.667[c]	4.40×10^{-3}	2.44×10^{2}
Styrene	0.0092	3.11	2.96×10^{-3}	1.64×10^{2}

[a] Assumed to be equivalent to ethylbenzene for calculational purposes.

[b] Henry's law constant could not be calculated, since acetone is completely miscible in water.

[c] Solubility of propylbenzene was used for calculational purposes.

[d] Calculated from Henry's law constant (except for acetone).

To convert Equation 6-23 to these units:

$$Q_i = (K_L)(A)(C_i)(1.81 \times 10^{-8}) \frac{\text{lb}}{\text{hr}} (A)\text{ft}^2(3600)$$

$$\frac{\text{hr}}{\text{sec}} \frac{(454)\text{g}}{\text{lb}} \frac{(10^9)\text{ng}}{\text{g}} \frac{\text{ft}^2}{(929)\text{cm}^3}$$

$$Q_i = (K_L)(C_i)(2.45 \times 10^{-3})$$

where Q_i is presented in ng/cm^2-sec.

It was desirable to express the final results in larger scale units. All final flux results are expressed in units of kg-compound/hectare-year. To convert the previous units into these, the following multiplication factors were used.

$$Qi(\text{kg/ha-yr}) = Qi(\text{ng-C/cm}^2\text{-sec}) \frac{MW}{MW_c} (31{,}500)$$

where:

MW = the molecular weight of the compound of interest

MW_c = the molecular weight of carbon in the compound.

SECTION 7

RESULTS

In this section, results of the overall project are presented and discussed. Examples of meteorological and VOC data, and summaries of run data collected at each site are included. The results of flux calculations on these data are presented and discussed. The predictive model was applied to data collected from primary treatment ponds at each of the sites and compared to experimental flux data from these ponds.

DATA PRESENTATION AND SUMMARY

The sampling matrices for tests which were performed at each site were presented in Section 5. Examples of meteorological and VOC measurement data are presented in this section, as well as run summaries for each site and an interpretation of these data. Because of the volume of data, detailed meteorological and VOC measurement data are presented in the Appendices.

Meteorological Data

Meteorological data were collected for 20 minutes prior to each sampling period and for 20 minutes during each period. Data collected prior to each sampling period were used to perform quality control tests to determine if proper meteorological conditions existed for sampling. The quality control functions are discussed in Section 8. An example of the meteorological data which were collected for each run is presented in Table 7-1. Data were sampled at one-second intervals and averaged to provide 2-minute and 20-minute average values. The remainder of the meteorological data and descriptions of the computer abbreviations used above each column are presented in Appendix A.

Flux calculations required input of the Richardson numbers, which were calculated from the slopes of temperature and wind speed with respect to height above the water surface. All 20-minute averages were recalculated to provide three significant figures. Quality control tests (see Section 8) indicated that normalization of these averages was a valid treatment. It was evident when examining the corrected temperature data that five of the six values obtained at height 5 were not consistent with the remainder of the data. Therefore, all temperature data collected at this height were not used for further data treatment.

TABLE 7-1. METEOROLOGICAL DATA COLLECTED AT SITE FB - RUN 2

Presampling

STATION 001 1559 03/16/82

TIME	TMP1 DGF	TMP2 DGF	TMP3 DGF	TMP4 DGF	TMP5 DGF	TMP6 DGF	WDRT DEG	WS1 MPH	WS2 MPH	WS3 MPH	WS4 MPH	WS5 MPH	WSR MPH	WSA TMPH	WDA DEG	WDAV DEG	WGUST MPH
1538	72	71	71	71	71	70	7	7	3	9	10	10	9	10	7	23	14
1540	72	71	71	71	71	70	12	8	5	9	11	10	12	11	12	19	14
1542	72	71	70	71	71	70	13	8	5	10	11	11	12	12	13	22	15
1544	72	71	70	71	71	70	15	8	5	10	11	11	12	11	15	32	14
1546	72	71	70	71	71	70	12	8	4	9	11	10	12	11	12	25	14
1548	72	71	70	71	71	70	15	8	5	10	11	11	12	11	15	33	14
1550	72	71	70	71	71	70	16	8	5	10	11	11	12	12	17	42	15
1552	71	70	70	71	71	69	18	8	5	10	12	11	13	12	18	32	15
1554	72	71	70	71	71	70	15	7	4	9	10	10	11	11	15	36	14
1556	72	71	70	71	71	70	14	7	2	9	10	10	11	10	14	43	14
AVG	72	71	70	71	71	70	2019	8	4	10	11	11	12	11	14	39	15

Sampling

STATION 001 1620 03/16/82

TIME	TMP1 DGF	TMP2 DGF	TMP3 DGF	TMP4 DGF	TMP5 DGF	TMP6 DGF	WDRT DEG	WS1 MPH	WS2 MPH	WS3 MPH	WS4 MPH	WS5 MPH	WSR MPH	WSA TMPH	WDA DEG	WDAV DEG	WGUST MPH
1600	72	71	70	71	71	70	12	7	4	9	11	10	12	11	12	23	13
1602	72	71	70	71	71	70	19	7	1	8	9	9	10	9	19	51	12
1604	72	71	71	71	72	70	24	7	4	9	11	10	12	11	24	31	14
1606	72	71	71	71	72	70	30	8	4	10	11	10	12	11	30	46	14
1608	72	71	71	72	72	71	29	7	4	9	11	10	11	11	29	53	13
1610	72	71	71	72	72	71	27	7	4	9	10	10	11	11	27	42	13
1612	72	71	71	72	72	71	29	8	4	10	11	10	11	11	29	52	14
1614	72	71	71	72	72	71	24	8	4	9	11	10	12	11	24	33	14
1616	72	71	71	72	72	70	20	7	3	9	10	10	11	11	20	44	14
1618	72	71	71	72	72	71	24	7	0	8	9	9	10	9	23	28	12
AVG	72	71	71	72	72	71	1997	7	3	9	10	10	11	11	24	68	14

For a description of column heading abbreviations, see Appendix A.

The slopes of temperature and wind speed as a result of height above the water surface, and the corresponding Richardson numbers are presented in Table 7-2. For calculation of Richardson numbers, all temperature data were converted to degrees Kelvin (K). The number of data points used for each slope measurement is presented in this table. As previously discussed, one temperature measurement was discarded for all runs. Also, because of inconsistencies with other wind speed data, wind speed measurements collected at height 2 were not used at site FB. The variations of temperatures with respect to height ranged from -0.0020 K/cm to -0.0041 K/cm and the variations of wind speed with respect to height ranged from 0.327 cm/sec-cm to 0.722 cm/sec-cm. Three different statistical tests were performed on each slope measurement. These were the computations of standard error, correlation coefficient (r) and T-value. The standard error is a measure of the data scatter (similar to a standard deviation). Standard errors were used as uncertainties associated with the slope measurements for calculation of overall errors associated with the corresponding Richardson numbers. The correlation coefficient is a measure of the linearity of the data (1.00 being a perfect line). Correlation coefficients ranged from 0.60 to 0.96 for temperature/height plots and from 0.79 to 0.96 for wind speed/height plots. The T-values were used to test the slopes for statistical difference from zero. Three of the six temperature/height slopes and five of the six wind speed/height slopes tested to be statistically different from zero within 95% confidence limits. The remaining slopes were all statistically different from zero within 80% confidence limits.

Richardson numbers and the errors associated with them are presented in the last two columns of Table 7-2. All of the Richardson numbers were greater than or equal to the quality control limit ($R \geq -0.1$). Standard errors listed for the Richardson numbers were generated using a Monte-Carlo computer method. This method involved regenerating the Richardson numbers 200 times for each run using Gaussian distributions for all parameter errors. For each of the 200 trials, sample estimates of the measured parameters used to calculate Richardson numbers (absolute temperature, temperature slope and wind speed slope) were computed. These estimates were then used to generate a new flux rate. Variabilities associated with these 200 trials were used as standard errors for the Richardson numbers.

Plots of temperature and wind speed as a function of height above the water surface are presented in Appendix A. These plots contain all data points which were collected and indicate which points were discarded.

VOC Species Data

The field sampling master logbooks and VOC species data for all air, water, blank, and quality assurance samples are presented in Appendix B. A sample data report is presented in Table 7-3. Each sample report is identified by a code number which describes the sample in the master logbook. Also listed at the top of each report are the site number (1 - FB, 2 = TB), site position (run 1, 2 or 3), date and time of sample collection, type of sample, container type, sampling height, and wind speed and temperature corresponding to the height at which the sample was collected. All species detected at

TABLE 7-2. STATISTICAL PARAMETERS USED IN CALCULATING RICHARDSON NUMBERS

	Temperature (K)			Temp (K) vs Sensor Ht (cm)					Wind speed (cm/sec) vs Sensor Ht (cm)					Richardson Number	
Site/Sample	n	Mean	Std. Error.	n	Slope Estimate	Std. Error	r	T-value	n	Slope Estimate	Std. Error	r	T-value	Estimate	Std. Error
FB-1	5	297.42	0.27	5	-0.0041	0.0007	0.96	-5.6	5	0.431	0.126	0.89	3.4	-0.072	0.098
FB-2	5	294.67	0.26	5	-0.0033	0.0014	0.81	-2.4	5	0.431	0.126	0.89	3.4	-0.059	0.129
FB-3	5	294.76	0.36	5	-0.0033	0.0026	0.60	-1.3	5	0.327	0.148	0.79	2.2	-0.104	0.384
TB-1	5	296.27	0.21	5	-0.0029	0.0009	0.87	-3.0	6	0.622	0.112	0.94	5.5	-0.024	0.014
TB-2	5	296.51	0.20	5	-0.0020	0.0014	0.64	-1.4	6	0.770	0.113	0.96	6.8	-0.011	0.009
TB-3	5	297.69	0.16	5	-0.0024	0.0004	0.96	-5.9	6	0.688	0.068	0.90	4.1	-0.017	0.019

n = number of observations

r = correlation coefficient

T-value is the t-statistic for testing the null hypothesis that the slope equals zero.
For n = $5/T_{.95}/\geq 3.2$; for n = $6/T_{.95}/\geq 2.8$; for n = $5/T_{.80}/\geq 1.2$

TABLE 7-3. EXAMPLE VOC SPECIES SAMPLE DATA REPORT

```
        VOC POND EMISSIONS:  SAMPLE DATA REPORT
-------------------------------------------------------------
  CODE NO.:     8              SAMPLE TYPE:  DUPLICATE CANISTER
  SITE NO.:  1                 CONTAINER TYPE:  RADIAN SS
  SITE POS.:  1                SAMPLING HEIGHT:  13 IN A
  DATE:  031682                WINDSPEEC:   5 MPH
  BEGIN:  10:18                TEMPERATURE:  77 F
  END:  10:38
-------------------------------------------------------------

                                            CONCENTRATION
     COMPOUND                                  (PPBV-C)
     --------                               -------------

 TOTAL C2                                        16.5
 DICHLOROMETHANE                                  6.0
 BUTERALDEHYDE                                    9.8
 2-METHYL-1-PENTENE                               7.2
 BENZENE                                         57.6
 TOLUENE                                         17.0
 3-METHYLHEPTANE                                  9.2
 M-XYLENE                                        11.4
 STYRENE                                         22.2
 N-DECANE                                         7.5
 N-UNDECANE                                       7.7
 DIETHYL ETHER                                   55.1
 INDENE                                          25.2
 METHYLHEXANONE                                  10.0
 UNID C9 ALKANE                                   6.6
 UNID C10 ALKANE                                 10.6
 UNID C10 ALKANE                                  7.2
 UNID C10 ALKANE                                  7.8
 UNID >C10 ALKANE                                10.7

 TOTAL ALKANES                                   83.8
 TOTAL ALKENES AND ALKYNES                        7.2
 TOTAL AROMATICS                                133.4
 TOTAL OXYGENATED HC                             74.9
 TOTAL CHLOR. UNSAT. HC                           0
 TOTAL CHLOR. SAT. HC                             6.0

 TOTAL NMHC                                     305.3
 % IDENTIFIED                                    85.9%
```

levels above 3 ppbv-C (parts per billion of carbon by volume) are presented along with the measured concentration.

The concentration unit which was used (ppbv-C) is commonly used for ambient air VOC studies. This unit reduces each compound to its volume content of carbon. For example, 1 ppbv of ethane, propane and benzene would be 2, 3, and 6 ppbv-C of each species, respectively. In the example presented, 57.6 ppbv-C of benzene corresponds to 9.6 ppbv of this species. The use of these units allows easy summation of chemical species into classes. In each sample report, totals are presented for alkanes, alkenes and alkynes, aromatics, oxygenated hydrocarbons, and saturated and unsaturated chlorinated hydrocarbons. Also, all species were summed to provide a total nonmethane hydrocarbon content (Total NMHC). All sample components which could not be identified by species were identified according to chemical class and boiling point range according to schemes discussed in Section 4. Also, ethane, ethylene and acetylene were grouped together as Total C_2 and propane and propylene were grouped together as Total C_3. The percentage of carbon in each sample which was identified by species is presented at the bottom of each report.

Run Summaries

Data summaries for each of the six test runs (three at each site) are presented in Tables 7-4 through 7-9. The heading of each table lists the site, site position, date and times of sampling. Measured parameter values are then presented for each of six mast samples, a duplicate mast sample at level 2, and the upwind sample, blank sample, and water sample for each test run. The sample code number is also provided to allow comparison with the sample data reports and sample log book in Appendix B. The container type, Radian or EPA canister, used for each sample is also listed since a contamination problem was observed in some of the canisters supplied by EPA. This problem will be discussed further in Section 8. The temperature and wind speed measured at each mast height are then presented. Finally, all VOC species or classes measured in at least three of the mast samples are presented along with their respsective concentrations.

Six blanks were collected for this study, three at each site. The three blanks from each site were averaged, and average species and class values are presented in Tables 7-4 to 7-9. Significant contamination was observed in the 1.0 L EPA canisters that were used for collection of blanks and upwind samples at site TB. This resulted in higher concentrations of some species appearing in blank and upwind samples than were in the mast samples. Data for these samples and blanks collected in these containers (Tables 7-7 through 7-9) should be interpreted with caution.

Data presented for the duplicate mast samples were all collected at sampling height 2. Data listed under mast position 2A were collected in Radian canisters, EPA canisters, or sorbent cartridges. In most cases, data for the duplicate samples were averaged. However, data for sorbent cartridges were not averaged with those from canisters due to blank problems encountered with the cartridges.

TABLE 7-4. RUN SUMMARY FOR SITE FB: RUN 1

SAMPLING DATE: 3/16/82 START TIME: 10:18 FINISH TIME: 10:38

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1[e]	2	2A	3	4	5	6		
SAMPLE #	001	033-035[a]	002	003	008	004	005	006	007	093,095[b]	--
CONTAINER TYPE[d]	EC	RC	RC	RC	RC	EC	EC	RC	RC	BT	--
TEMPERATURE	--	--	77.3	76.5	76.5	75.9	75.8	76.2[c]	74.3	77	°F
WIND SPEED	--	--	6	5[c]	5[c]	8	9	9	10	--	mph
TOTAL C_2	18.9	3.9	--	41.2	17.3	21.3	22.9	10.5	19.4	1.6	ppbv-C
TOTAL C_3	--	--	--	--	--	--	7.0	9.1	5.4	0.5	
N-BUTANE	--	--	--	--	--	6.2	9.9	6.2	--	--	
DICHLOROMETHANE	12.9	--	--	9.3	5.5	8.5	8.2	5.2	10.1	1.5	
BUTERALDEHYDE	14.0	1.1	--	12.8	9.4	13.7	22.8	38.8	28.3	--	
BUTANONE	13.7	--	--	--	--	9.4	12.6	5.0	8.5	--	
BENZENE	11.2	6.3	--	47.0	52.3	34.5	49.8	35.9	14.1	8.2	
3-PENTANONE	7.1	--	--	--	--	6.7	9.2	14.2	--	0.1	
TOLUENE	11.5	7.7	--	15.6	15.0	15.5	17.7	12.2	10.2	1.0	
3-METHYLHEPTANE	9.4	--	--	8.7	8.6	6.5	8.7	5.0	21.3	--	
M-XYLENE	45.5	1.4	--	10.9	11.1	14.5	11.8	10.3	12.0	0.1	
STYRENE	9.1	--	--	17.5	20.7	17.9	14.9	15.4	14.2	2.9	
4-NONENE	7.0	--	--	--	--	5.0	13.9	5.0	8.5	--	
B-PINENE	--	1.1	--	--	--	11.6	--	8.8	15.9	0.1	
N-DECANE	46.3	5.7	--	6.6	10.7	15.7	8.2	2.0	2.0	0.1	
N-UNDECANE	20.9	3.0	--	8.9	6.3	21.6	13.0	--	2.0	0.1	

(Continued)

TABLE 7-4. (Continued)

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE 1^e	2	2A	3	4	5	6	WATER CONC. ng-C/mL	UNITS
SAMPLING DATE: 3/16/82 START TIME: 10:18 FINISH TIME: 10:38											
DIETHYL ETHER	34.0	--	--	41.7	52.2	33.7	22.2	44.6	11.8	3.6	
2-METHYL-3-PENTANONE	8.6	--	--	--	--	5.5	6.8	5.0	--	0.1	
INDENE	--	--	--	21.0	25.2	23.8	15.2	--	5.2	5.3	
METHYLHEXANONE	25.6	--	--	8.3	8.6	15.5	20.5	15.0	5.3	--	
ALKANES	506.2	28.4	--	89.7	86.2	373.3	141.0	255.1	109.9	4.8	
ALKENES & ALKYNES	99.9	8.6	--	10.7	27.4	45.4	20.9	56.1	24.4	4.2	
AROMATICS	156.4	23.3	--	117.1	124.5	106.2	109.4	104.6	55.7	26.1	
OXYGENATED HC	112.5	2.4	--	62.9	70.2	84.5	94.1	122.6	69.8	4.3	
CHLORINATED SATURATED HC	12.9	6.4	--	9.3	5.5	8.5	8.2	13.2	10.1	2.3	
TNMHC	894.6	72.8	--	289.7	313.8	617.9	373.6	551.6	269.9	44.2	

[a] Average species concentrations for blank samples 033, 034, 035.

[b] Average species concentrations for water samples 093, 095.

[c] Data not used for flux calculations.

[d] EC = EPA SS canister, RC = Radian SS canister, SC = Sorbent Cartridge, EA = EPA aluminum canister.

[e] Sample lost due to moisture in probe.

--As applied to species = Below detection limits (3 ppbv-C)

TABLE 7-5. RUN SUMMARY FOR SITE FB: RUN 2

SAMPLING DATE: 3/16/82 START TIME: 15:38 FINISH TIME: 15:58

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1[c]	2	2A	3	4	5	6		
SAMPLE #	009	033-035[a]	011	012	017	013	014	015	016	093,095[b]	--
CONTAINER TYPE[d]	EC	RC	RC	RC	RC	EC	EC	RC	RC	BT	--
TEMPERATURE	--	--	72.7	71.0	71.0	70.9	70.6	71.0[c]	69.8	76	°F
WIND SPEED	--	--	7	3[c]	3[c]	9	10	10	11	--	mph
TOTAL C_2	24.7	3.9	39.1	26.3	27.0	51.7	22.3	140.0	33.5	1.6	ppbv-C
TOTAL C_3	8.4	--	--	10.7	10.9	17.4	9.1	--	--	0.5	
N-BUTANE	4.2	--	--	5.4	6.6	6.2	11.1	--	--	--	
T-2-BUTENE	--	--	--	11.4	7.8	6.9	6.6	--	--	0.1	
BUTERALDEHYDE	44.3	1.1	--	11.2	6.7	36.9	34.1	--	--	--	
3-METHYLPENTANE	7.5	--	--	9.7	14.4	8.3	13.6	--	--	0.2	
BUTANONE	16.9	--	--	65.8	31.1	6.3	6.9	--	--	--	
BENZENE	12.3	6.3	32.4	58.5	51.6	28.6	26.5	14.4	23.4	8.2	
3-PENTANONE	--	--	--	12.6	13.2	8.3	4.3	--	--	0.1	
TOLUENE	5.2	7.7	10.4	11.4	11.3	11.5	5.6	8.1	--	1.0	
DIBROMOCHLOROMETHANE	--	--	--	3.3	--	32.1	19.2	--	--	--	
M-XYLENE	4.0	1.4	--	6.7	8.9	8.6	3.5	--	--	0.1	
STYRENE	6.1	--	11.3	8.3	10.3	13.7	--	--	--	2.9	
DIETHYL ETHER	--	--	13.7	55.5	56.1	36.9	31.1	5.0	8.3	3.6	
2-METHYL-3-PENTANONE	7.7	--	--	6.4	6.7	--	9.8	--	18.5	0.1	
INDENE	--	--	26.1	8.5	21.8	9.6	--	--	--	5.3	
METHYLHEXANONE	8.4	--	--	21.5	13.4	10.7	8.0	--	--	--	

(Continued)

TABLE 7-5. (Continued)

ALKANES	75.4	28.4	49.1	101.5	94.6	174.6	81.0	140.0	59.2	4.8
ALKENES & ALKYNES	5.0	8.6	--	40.4	25.9	31.6	21.2	--	--	4.2
AROMATICS	42.6	23.3	80.2	103.0	115.5	83.2	39.8	22.5	23.4	26.1
OXYGENATED HC	108.5	2.4	13.7	202.3	144.4	117.3	144.7	5.0	26.8	4.3
CHLORINATED SATURATED HC	--	6.4	--	3.3	--	39.0	19.2	--	--	2.3
TNMHC	231.5	72.8	148.0	450.4	380.4	445.7	305.9	167.5	109.4	44.2

---

[a] Average species concentrations for blank samples 033,034,035.

[b] Average species concentrations for water samples 093,095.

[c] Data not used for flux calculations.

[d] EC = EPA S.S. canister, RC= Radian S.S. canister, SC = Sorbent Cartridge, EA = EPA aluminum canister.

--As applied to species = Below detection limits (3ppbv-C)

TABLE 7-6. RUN SUMMARY FOR SITE FB: RUN 3

SAMPLING DATE: 3/16/82 START TIME: 17:30 FINISH TIME: 17:50

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1	2	2A[c]	3	4	5	6		
SAMPLE #	019	033-035[a]	020	021	27	022	023	024	025	093,095[b]	--
CONTAINER TYPE[d]	EC	RC	RC	RC	SC	EC	EC	RC	RC	BT	--
TEMPERATURE	--	--	73.7	71.0	71.0	70.5	70.4	71.7[c]	70.2	76	°F
WIND SPEED	--	--	8	2[c]	2[c]	9	11	10	11	--	mph
TOTAL C_2	25.0	3.9	19.5	225.6	601.6	201.8	33.3	59.5	48.6	1.6	ppbv-C
TOTAL C_3	7.6	--	12.5	11.5	136.6	15.2	11.4	13.6	9.0	0.5	
CHLOROMETHANE	--	6.4	14.8	5.0	4.8	2.7	11.9	10.0	--	--	
N-BUTANE	6.7	--	--	--	37.7	7.5	15.2	7.0	--	--	
2-METHYL-2-BUTENE	4.6	--	9.8	8.4	--	--	10.4	--	--	--	
DICHLOROMETHANE	--	--	--	--	--	19.7	--	12.5	18.8	1.5	
T-2-HEXENE	--	--	6.0	--	--	4.7	4.1	--	--	--	
BENZENE	15.3	6.3	91.2	43.4	95.5	69.1	62.4	64.6	54.2	8.2	
3-PENTANONE	5.6	--	8.4	3.2	2.8	7.2	6.7	7.3	12.0	0.1	
TOLUENE	14.8	7.7	14.5	11.2	55.3	15.1	8.7	14.8	13.0	1.0	
3-METHYLHEPTANE	--	--	--	--	--	13.7	--	6.7	7.4	--	
ETHYLBENZENE	--	--	5.0	--	5.4	23.6	5.2	6.3	9.5	0.2	
M-XYLENE	3.3	1.4	8.6	7.0	--	8.9	10.0	9.1	9.0	0.1	
STYRENE	--	--	14.5	13.8	--	24.7	13.1	15.7	10.8	2.9	
N-PROPYLBENZENE	4.1	--	5.3	2.2	0.9	6.0	2.2	--	--	0.1	
1-DECENE	--	--	5.3	--	--	8.0	--	--	9.1	0.1	
1,2,3-TRIMETHYLBENZENE	--	--	22.7	6.0	--	--	12.0	21.3	--	--	
DIETHYL ETHER	--	--	68.4	45.1	8.2	45.3	46.7	49.6	24.3	3.6	
METHYLBUTANONE	7.0	--	25.2	7.6	17.9	33.9	18.7	26.4	20.3	--	
2-METHYL-3-PENTANONE	6.1	--	31.1	10.4	4.3	29.7	19.6	31.1	16.8	0.1	
METHYLSTYRENE	--	--	7.5	--	--	8.2	--	--	16.7	0.2	
INDENE	--	--	13.0	20.1	--	20.9	15.6	21.6	18.9	5.3	

(Continued)

TABLE 7-6. (Continued)

ALKANES	125.2	28.4	201.6	265.1	1132.7	342.3	90.1	254.0	88.5	4.8
ALKENES & ALKYNES	41.3	8.6	33.2	50.5	117.1	69.3	82.5	62.2	19.2	4.2
AROMATICS	37.5	23.3	194.4	121.3	166.9	202.3	134.2	180.2	132.1	26.1
OXYGENATED HC	76.2	2.4	133.1	72.8	198.2	126.5	104.3	119.4	73.4	4.3
CHLORINATED UNSATURATED HC	--	3.6	33.1	6.5	2.1	19.8	14.5	6.4	--	2.4
CHLORINATED SATURATED HC	--	6.4	33.5	30.3	20.4	43.4	27.7	22.5	18.8	2.3
TNMHC	280.2	72.8	628.9	546.5	1637.4	803.6	453.3	644.7	332.0	44.2

[a] Average species concentrations for blank samples 033,034,035.

[b] Average species concentrations for water samples 093,095.

TABLE 7-7. RUN SUMMARY FOR SITE TB: RUN 1

SAMPLING DATE: 3/19/82 START TIME: 10:17 FINISH TIME: 10:37

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1	2	2A	3	4^c	5	6		
SAMPLE #	061	050-052^a	053	054	059	055	056	057	058	077, 078^b	--
CONTAINER TYPE^d	EC	EC	RC	RC	EC	EC	EC	RC	RC	BT	--
TEMPERATURE	--	--	75.1	73.8	73.8	73.9	73.9	73.4^c	72.7	71	°F
WIND SPEED	--	--	12	[illegible]	14	15	15	16	18	--	mph
TOTAL C_2	126.6	73.2	59.1	52.8	88.6	16.7	68.6	59.0	60.0	1.1	ppbv-c
TOTAL C_3	19.8	12.0	--	--	6.8	--	11.1	5.7	4.7	0.8	
N-BUTANE	14.8	10.2	--	7.5			29.8	3.9	3.2	1.2	
ACETONE	16.4	--	13.5	5.6	31.2	21.4	--	6.5	10.9	20.5	
ISOBUTERALDEHYDE	18.4	1.1	--	3.8	4.9	--	23.2	--	12.9	0.1	
BUTERALDEHYDE	16.5	6.1	--	7.9	14.4	--	57.9	13.0	13.0	1.6	
3-METHYLPENTANE	6.3	5.3	5.2	3.1	--	8.0	10.5	5.0	9.3	2.3	
BENZENE	16.3	7.2	6.6	11.6	13.9	--	19.4	4.3	--	14.5	
CYCLOHEXANE	420.4	32.7	6.1	3.2	7.0	--	13.0	3.4	--	14.4	
TOLUENE	32.7	15.0	7.5	6.4	9.9	--	4.1	7.3	6.2	9.1	
O-XYLENE	--	5.8	--	6.1	10.5	--	--	8.7	6.3	1.1	
1-NONENE	37.8	4.0	--	6.9	8.5	--	9.2	6.2	4.1	--	
N-PROPYLBENZENE	14.9	7.6	--	3.2	5.8	4.6	6.0	--	--	0.6	
O-ETHYLTOLUENE	--	1.6	4.6	3.9	4.7	--	5.5	3.9	--	4.8	
N-DECANE	--	9.9	7.4	--	--	--	6.2	3.2	--	3.3	
DIETHYL ETHER	31.0	6.8	--	6.1	12.7	10.0	23.5	--	--	6.1	

(Continued)

TABLE 7-7. (Continued)

ALKANES	1122.9	230.0	77.8	91.2	117.1	61.5	237.5	92.9	90.9	87.2
ALKENES & ALKYNES	236.4	45.0	14.8	18.3	23.3	--	118.7	15.8	21.7	49.2
AROMATICS	163.3	111.3	22.8	37.6	60.5	12.0	115.0	27.7	16.4	201.4
OXYGENATED HC	137.7	39.8	17.8	35.3	81.3	31.4	157.0	24.1	42.4	45.9
CHLORINATED SATURATED HC	--	21.1	--	--	--	6.4	15.6	--	8.4	1.0
TNMHC	1660.3	448.7	133.2	182.4	282.2	111.3	643.8	160.5	179.8	395.6

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[a] Average species concentrations for blank samples 050, 051, 052.

[b] Average species concentrations for water samples 077, 078.

[c] Data not used for flux calculations.

[d] EC=EPA SS canister, RC=Radian SS canister, SC=Sorbent cartridge, EA=EPA Aluminum canister.

-- As applied to Species = Below detection limits (3 ppbv-C)

TABLE 7-8. RUN SUMMARY FOR SITE TB: RUN 2

SAMPLING DATE: 3/16/82 **START TIME:** 10:50 **FINISH TIME:** 11:10

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1	2	2A[e]	3[c]	4	5	6		
SAMPLE #	080	050-052 [a]	063	064		005	066	007	068	077-078 [b]	--
CONTAINER TYPE[d]	EA	EC	RC	RC		EC	EC	RC	RC	BT	--
TEMPERATURE	--	--	75.7	74.2		74.0	74.0	74.5[c]	73.7	71	°F
WIND SPEED	--	--	13	15		16	17	18	20	--	mph
TOTAL C_2	116.3	73.2	36.7	38.3	--	69.9	44.4	31.9	34.2	1.1	ppbv-C
TOTAL C_3	11.0	12.0	3.6	--	--	18.5	4.8	3.2	--	0.8	
ACETONE	--	--	33.0	11.1	--	17.9	12.1	11.6	9.2	20.5	
ISOBUTERALDEHYDE	4.7	1.1	15.3	--	--	--	3.4	--	14.2	0.1	
CYCLOPENTENE	--	--	5.2	--	--	6.0	--	4.3	7.3	0.4	
BUTERALDEHYDE	--	6.1	6.0	4.3	--	23.0	12.0	11.8	10.0	1.6	
3-METHYLPENTANE	4.2	5.3	6.7	3.0	--	16.4	4.8	6.2	8.4	2.3	
1-HEXENE	6.9	1.8	3.9	4.5	--	10.5	4.2	3.5	3.9	0.3	
3-PENTANONE	3.6	3.1	3.1	3.0	--	15.1	5.9	5.5	5.7	9.7	
TOLUENE	13.7	15.0	4.9	4.6	--	32.4	5.0	5.8	4.7	9.1	
3-METHYLHEPTANE	--	--	3.2	--	--	--	4.2	4.0	4.1	--	
O-XYLENE	--	5.8	6.5	--	--	13.7	6.8	--	--	1.1	
1-NONENE	--	4.0	4.1	4.4	--	7.8	3.9	--	6.7	--	
A-PINENE	--	--	3.0	--	--	25.1	3.0	5.3	4.5	0.7	
O-ETHYLTOLUENE	--	1.6	--	4.1	--	13.5	4.8	--	--	4.8	
DIETHYL ETHER	--	6.8	6.2	7.0	--	6.8	8.5	8.1	--	6.1	

(Continued)

TABLE 7-8. (Continued)

2-METHYL-3-PENTANONE	--	1.6	3.4	--	--	11.1	3.2	3.0	6.5	0.3
ALKANES	260.4	230.0	59.6	41.3	--	357.3	83.2	96.1	64.6	87.2
ALKENES & ALKYNES	64.4	45.0	16.[illegible]	8.9	--	99.3	33.6	20.3	31.1	49.2
AROMATICS	73.7	111.3	21.4	8.7	--	607.6	35.8	14.5	8.1	201.4
OXYGENATED HC	80.1	39.8	67.0	25.4	--	118.8	53.9	40.0	51.2	45.9
TNMHC	478.6	448.7	164.2	84.3	--	1199.3	206.5	170.9	158.2	395.6

[a] Average species concentrations for blank samples 050, 051, 052.

[b] Average species concentrations for water samples 77, 78.

[c] Data not used for flux calculations.

[d] EC=EPA SS canister, RC=Radian SS canister, SC=Sorbent cartridge, EA=EPA Aluminum cannister.

[e] Duplicate sample not collected.

-- As applied to species = Below detection limits (3 ppbv-C)

TABLE 7-9. RUN SUMMARY FOR SITE TB: RUN 3

SAMPLING DATE: 3/16/82 START TIME: 14:06 FINISH TIME: 14:26

PARAMETER MEASURED	UPWIND VALUE	BLANK VALUE	MAST VALUE							WATER CONC. ng-C/mL	UNITS
			1	2	2A[c]	3	4	5	6		
SAMPLE #	081	050-052[a]	070	071	076	072	073	074	075	077, 078[b]	--
CONTAINER TYPE[d]	EA	EC	EA	EA	SC	EA	EA	EA	EA	--	--
TEMPERATURE	--	--	77.2	76.8	76.8	76.5	76.2	77.1[e]	75.5	73	°F
WIND SPEED	--	--	15	18	18	19	19	20	22	--	mph
TOTAL C_2	106.1	73.2	38.3	30.6	46.0	68.4	47.7	64.8	25.3	1.1	ppbv-C
TOTAL C_3	14.0	12.0	--	--	73.5	12.1	--	14.1	4.4	0.8	
ACETALDEHYDE	77.4	8.9	150.3	12.2	11.4	79.5	10.0	93.7	81.2	2.9	
ISOBUTENE + 1-BUTENE	11.6	8.7	15.1	15.5	11.4	32.7	14.6	24.8	--	2.1	
N-BUTANE	--	10.2	5.5	--	23.2	9.3	--	8.6	6.2	1.2	
ISOPENTANE	6.5	11.0	4.0	5.0	11.5	14.6	7.3	12.2	--	0.7	
ACETONE	--	--	237.0	18.0	21.3	4.7	6.5	5.2	--	20.5	
N-PENTANE	--	6.6	--	3.4	--	6.3	11.8	3.6	--	0.3	
T-2-PENTENE	11.8	2.8	11.8	4.2	--	9.8	7.3	--	--	0.1	
BUTERALDEHYDE	--	6.1	3.5	--	--	5.7	4.7	4.3	6.0	1.6	
BUTANONE	12.6	1.7	4.4	--	18.4	16.1	6.1	12.8	3.1	1.8	
1-HEXENE	12.4	1.8	3.9	--	3.5	9.2	--	--	3.7	0.3	
1,1,1-TRICHLOROETHANE	--	--	6.9	--	10.7	3.2	--	3.6	--	--	
BENZENE	21.4	7.2	7.6	4.2	17.1	9.8	3.0	6.2	8.0	14.5	
CYCLOHEXANE	--	32.7	8.7	5.5	36.6	4.7	3.6	3.0	--	14.4	
3-PENTANONE	28.0	3.1	7.9	9.1	8.7	3.0	9.6	5.5	7.1	9.7	
TOLUENE	35.9	15.0	8.7	17.7	8.0	21.4	16.0	36.2	29.8	9.1	
ETHYLBENZENE	86.5	39.0	--	7.6	--	20.5	33.8	50.3	8.0	10.4	

(Continued)

TABLE 7-9. (Continued)

P-XYLENE	--	--	3.1	4.6	--	10.4	--	--	20.6	1.0
O-XYLENE	--	5.8	4.7	6.9	--	16.7	7.4	17.6	--	1.1
ISOPROPYLBENZENE	11.5	8.7	27.5	3.7	--	25.3	6.1	98.3	23.7	0.5
A-PINENE	--	--	--	--	--	3.7	4.9	14.2	--	0.7
M-ETHYLTOLUENE	15.1	4.0	4.4	--	3.7	7.4	9.9	--	5.5	0.9
P-ETHYLTOLUENE	7.3	1.7	--	--	--	--	5.0	14.3	12.8	0.5
1,3,5-TRIMETHYLBENZENE	19.3	1.2	3.6	--	--	16.8	10.4	--	30.9	0.6
O-ETHYLTOLUENE	114.8	1.6	5.8	7.1	1.8	30.9	62.2	21.5	--	4.8
B-PINENE	10.6	1.3	--	--	--	4.6	5.7	26.7	--	0.8
1,4-DICHLOROBENZENE	26.2	--	26.4	5.9	--	21.9	22.6	--	--	--
N-DECANE	43.7	9.9	8.8	4.5	1.8	14.7	23.3	6.7	--	3.3
M-DIETHYLBENZENE	--	--	--	--	--	--	10.9	32.1	4.5	2.0
N-UNDECANE	--	5.1	13.4	4.0	2.2	15.5	--	--	--	5.3
METHYLBUTANONE	--	3.1	--	--	15.4	9.7	4.0	13.7	5.2	--
2-METHYL-3-PENTANONE	--	1.6	--	--	2.0	5.5	6.5	4.2	3.3	0.3
METHYLSTYRENE	--	--	8.3	--	2.7	--	24.4	26.4	--	1.0
INDENE	--	--	--	--	--	--	7.1	24.0	9.0	20.6
ALKANES	445.9	230.0	106.9	91.1	297.8	367.8	222.1	411.8	133.7	87.2
ALKENES & ALKYNES	408.6	45.0	34.5	19.7	67.3	106.8	216.3	318.0	79.1	49.2
AROMATICS	576.2	111.3	73.7	51.8	37.2	159.2	238.4	365.1	163.9	201.4
OXYGENATED HC	125.7	39.8	403.1	39.3	84.7	129.8	47.4	143.8	105.9	45.9
CHLORINATED UNSATURATED HC	39.4	1.5	26.4	5.9	4.7	35.0	27.6	3.1	5.2	10.8
CHLORINATED SATURATED HC	--	21.1	6.9	--	52.6	3.2	--	3.6	--	1.0
TNMHC	1595.8	448.7	651.5	207.8	544.3	801.8	751.8	1245.4	487.8	395.6

[a] Average species concentrations for blank samples 050, 051, 052.

[b] Average species concentrations for water samples 077, 078.

[c] Data not used for flux calculations.

[d] EC = EPA SS canister, RC = Radian SS canister, SC = Sorbent cartridge, EA = EPA aluminum canister.

--As applied to species = Below detection limits (3 ppbv-C).

Because of the loss of water samples collected simultaneously with mast samples, data from water samples collected at a later date at site FB were used. The inlet and outlet water samples for site TB (Tables 7-7 through 7-9) were used for this site. Species concentrations for these were averaged and used for predictive modeling. For site FB (Tables 7-4 through 7-8), the mast air samples were collected on March 16, 1982 and additional water samples were collected on April 28, 1982. Data presented for water samples from this site are averages of the inlet and outlet pond concentrations from the latter date.

VOC SPECIES FLUX RESULTS

Data presented in the preceding section were used to calculate flux rates for VOC species and classes using the Concentration-Profile (C-P) technique. Methods used for calculating flux rates were discussed in Section 6. The temperature and VOC species logarithmic profile results and corresponding chemical flux rates are presented in Table 7-10. The statistical tests used for each plot were the same as those used for the data presented in Table 7-2 and discussed in the section above, Data Presentation and Summary. Flux rates were calculated on the basis of carbon content of each species. For site FB, rates were calculated for four species--benzene, diethyl ether, indene, and styrene--and for total aromatics as a class. For site TB, flux rates were calculated for three species, benzene, acetone and cyclohexane. These species were chosen on the basis of manual inspection of concentrations at the six mast levels, and species concentrations in water, blank and upwind samples. Data used in calculating flux rates included the Richardson numbers presented in Table 7-2, VOC species data and wind speed data presented in Tables 7-4 through 7-9, logarithmic height profiles for wind speed and VOC species concentrations presented in Table 7-10, and species diffusivity corrections. Diffusivity corrections (DB_1/DA_1) for the species which were discussed are presented in Table 7-11. The diffusivity correction listed for the aromatic class is that for ethylbenzene.

The number of data points used for wind speed and VOC species profiles is listed in Table 7-10. The wind speed measurements which were deleted are discussed in the preceding section. Several mast samples were also deleted because of probable contamination. These are noted in Tables 7-4 to 7-9. Some VOC species were not observed in all six mast samples. In these cases, the species was given a value of one-half the detection limit (1.5 ppbv-C) for the lowest height sample which the species was not detected in, and higher samples were ignored if there was no measured value. The distribution of values between zero and the detection limit was assumed to have a normal distribution with a mean of one-half the detection limit. Plots of wind speed and chemical species concentrations as a function of logarithmic sensor height are presented in Appendix C. These plots contain all data points and indicate those which were deleted.

Because of the complexity of the equation for flux rates, a closed-form mathematical expression for flux variabilities was not used. Instead, the Monte Carlo method used for Richardson numbers was also used to calculate standard errors for flux rates. Flux rates were regenerated 200 times by using Gaussian distributions of each input parameter based on standard errors

TABLE 7-10. CALCULATED CHEMICAL FLUX RATES AND STATISTICAL REGRESSION PARAMETERS

	Wind Speed (cm/sec) vs Ln Sensor Ht (cm)						Chemical Conc (ng - C/cm^3) vs Ln Sensor Ht (cm)					Flux Rate (ng - C/cm^2 - sec)	
Site/Sample	n	Slope Estimate	Std. Error	r	T-value	Species	n	Slope Estimate	Std. Error	r	T-value	Estimate	Std. Error
FB-1	5	73.0	7.7	0.98	9.5	Benzene	5	-0.0054	0.0030	0.73	-1.8	0.0679	0.0544
						Diethyl Ether	5	-0.0048	0.0034	0.63	-1.4	0.0604	0.0543
						Indene	4	-0.0039	0.0010	0.95	-4.1	0.0357	0.0163
						Styrene	5	-0.0010	0.0002	0.94	-4.8	0.0104	0.0044
						Total Aromatics	5	-0.0104	0.0045	0.80	-2.3	0.1169	0.0643
FB-2	5	73.0	7.7	0.98	9.5	Benzene	5	-0.0066	0.0024	0.84	-2.7	0.0761	0.0500
						Diethyl Ether	5	-0.0103	0.0017	0.96	-6.0	0.1207	0.0582
						Indene	3	-0.0048	0.0008	0.99	-6.4	0.0410	0.0230
						Styrene	3	-0.0026	0.0035	0.59	-0.73	0.0250	0.0440
						Total Aromatics	5	-0.0192	0.0031	0.96	-6.3	0.2001	0.0914
FB-3	5	56.2	17.4	0.88	3.2	Benzene	6	-0.0030	0.0023	0.55	-1.3	0.0336	0.0426
						Diethyl Ether	6	-0.0039	0.0014	0.82	-2.8	0.0442	0.0558
						Indene	6	0.0007	0.0005	0.57	1.4	-0.0054	0.0065
						Styrene	6	-0.0003	0.0008	0.16	-0.33	0.0025	0.0090
						Total Aromatics	6	-0.0042	0.0057	0.35	-0.74	0.0425	0.0902
TB-1	6	99.5	12.6	0.97	7.9	Benzene	4	-0.0007	0.0004	0.77	-1.7	0.0077	0.0049
						Acetone	5	-0.0008	0.0010	0.44	-0.85	0.0121	0.0152
						Cyclohexane	4	-0.0005	0.0001	0.95	-4.5	0.0051	0.0015
TB-2	6	123.7	7.2	0.99	17	Benzene	2	-0.0003	**	1.0	—	0.0032	0.0227
						Acetone	5	-0.0026	0.0009	0.84	-2.7	0.0397	0.0138
						Cyclohexane	2	-0.0006	**	1.0	—	0.0058	0.0215
TB-3	6	114.3	16.3	0.96	7.0	Benzene	6	-0.00004	0.0004	0.04	-0.08	0.0004	0.0053
						Acetone	5	-0.0027	0.0010	0.84	-2.7	0.0422	0.0207
						Cyclohexane	5	-0.0008	0.00005	0.99	-17	0.0087	0.0019

**A standard error of 0.002 ng - C/cm^3 was used in computing the standard error of the flux rate estimate.

Notations: n = number of observations
r = correlation coefficient
T-value is the t-statistic for testing the null hypothesis that the slope equals zero.

TABLE 7-11. DIFFUSIVITY CORRECTIONS USED IN FLUX CALCULATIONS

Species	Diffusivity Correction
Benzene	0.352
Diethyl Ether	0.356
Indene	0.220
Styrene	0.264
Acetone	0.498
Cyclohexane	0.268
Total Aromatics*	0.301

*Value for ethylbenzene

for each parameter. From these 200 flux rates, a mean value and standard deviation were calculated for each VOC species. These standard errors are listed in Table 7-10.

VOC species flux rates for runs one and two at site FB were very similar. However, flux rates for run three were lower. Flux rates observed at site TB were consistently lower than those from site FB.

PREDICTIVE MODEL RESULTS AND COMPARISONS

Results of applying the predictive model to estimate VOC species emission rates are discussed in this section. This consists of a comparison of predicted and measured flux rates.

Model Comparisons to Site Data

The predictive model described in Section 6 was applied to the two sites and compared to measured flux rates calculated using the C-P technique. The derived rate constants for the predictive model are presented in Table 7-12. Results of predicted and measured flux rates for the secondary ponds are presented in Table 7-13. Predicted flux rates were calculated from the maximum inlet water concentration and the mean inlet-outlet concentration at site FB. For site TB, the inlet and outlet concentrations did not vary significantly, so predicted flux rates were calculated for mean species concentrations only. The species concentrations which were used are listed in parentheses under the predicted flux rates. For comparison, the three measured flux rates and standard errors are also listed for each species. The 95% confidence limits ($\pm 2\sigma$) are listed in parentheses under each measured flux rate.

The predicted flux rates for total aromatics were calculated using diffusivities for ethylbenzene. Even though the concentrations for total

TABLE 7-12. DERIVED RATE CONSTANTS FOR THE PREDICTIVE MODEL

Site FB	MW (lb/lb mole)	D_{T_2} (ft^2/hr)	$(k_L)_c$ (lb mole/ft^2hr)	$(k_g)_c$ (lb mole/ft^2hr)	$(k_L)_T$ (lb mole/ft^2hr)	$(k_g)_T$ (lb mole/ft^2hr)
Benzene	78	0.370	0.466	0.203	511	3.45
Diethyl ether	74	0.374	0.479	0.204	518	3.66
Total Aromatics	106	0.316	0.400	0.182	474	2.35
Indene	120	0.231	0.376	0.148	459	1.77
Styrene	104	0.277	0.404	0.167	476	2.24
Site TB						
Benzene	78	0.370	1.12	0.313		
Acetone	58	0.523	1.30	0.394		
Cyclohexane	84	0.281	1.08	0.268		

$k_{Lc} = (4.12)/(MW_i)^{.5}$ for site FB; $k_{Lc} = (9.87)/(MW_i)^{.5}$ for site TB

$k_{gc} = (.426)(D_{T_2})^{.67}$ for site TB; $k_{gc} = (0.658)(D_{T_2})^{.67}$ for site TB

$k_{LT} = (1.52 \times 10^3)/(MW)^{.25}$

$k_{gT} = (443)(D_i)^{.5}/MW_i$

TABLE 7-13. RESULTS OF PREDICTED AND MEASURED FLUX RATES[a] FOR SECONDARY WASTEWATER PONDS

Species or Class	Predicted Flux (max. inlet conc.)[b]	Predicted Flux (ave. conc.)[c]	MEASURED FLUX[d]		
			Run 1	Run 2	Run 3
Site = FB					
Benzene	0.409 (16.1)	0.208 (8.2)	0.0679 ± 0.0544 (0 - 0.174)	0.0761 ± 0.0500 (0 - 0.174)	0.0336 ± 0.0426 (0 - 0.117)
Diethyl Ether	0.0194 (2.7)	0.0266 (3.7)	0.0604 ± 0.0543 (0 - 0.167)	0.1207 ± 0.0582 (0.0066 - 0.235)	0.0442 ± 0.0558 (0 - 0.154)
Indene	0.177 (10.6)	0.0889 (5.3)	0.0357 ± 0.0163 (0.0037 - 0.0677)	0.0410 ± 0.0230 (0 - 0.0861)	- 0.0054 ± 0.0065 (0 - 0.0073)
Styrene	0.0892 (5.7)	0.0438 (2.8)	0.0104 ± 0.0044 (0.0018 - 0.0190)	0.0250 ± 0.0440 (0 - 0.111)	0.0025 ± 0.0090 (0 - 0.0202)
Total Aromatics	1.13 (50.2)	0.586 (26.1)	0.1169 ± 0.0643 (0 - 0.243)	0.2001 ± 0.0914 (0.0214 - 0.380)	0.0425 ± 0.0902 (0 - 0.219)
Site = TB					
Benzene	[e]	0.0394 (14.5)	0.0077 ± 0.0049 (0 - 0.0173)	0.0032 ± 0.0227 (0 - 0.0476)	0.0004 ± 0.0053 (0 - 0.0109)
Cyclohexane	[e]	0.0381 (14.4)	0.0051 ± 0.0015 (0.0022 - 0.0081)	0.0058 ± 0.0215 (0 - 0.0480)	0.0087 ± 0.0019 (0.0049 - 0.0125)
Acetone	[e]	0.00458 (20.5)	0.0121 ± 0.0152 (0 - 0.0420)	0.0397 ± 0.0138 (0.0126 - 0.0668)	0.0422 ± 0.0207 (0.0017 - 0.0827)

[a] All flux rates presented in ng-C/cm^2-Sec

[b] Predicted flux using species concentration at inlet end of pond.

[c] Predicted flux using average species concentration at inlet and outlet ends of pond.

[d] Measured flux ± standard error and 95% confidence interval in parenthesis.

[e] Prediction not performed on inlet concentration since this did not differ significantly from average concentration.

aromatics were much higher than those for benzene, the predicted benzene flux was significantly higher than that for total aromatics. This indicates that the predictive model has limited applications when applied to a VOC class or total NMHC data. It should be noted that even though chemical class emissions can be measured, the predictive model was not intended for application to chemical classes.

A summary of the predicted and measured VOC flux rates is presented in Table 7-14. For these data, the three measured flux rates for each species or class at each site were averaged, and standard errors were pooled to obtain an overall standard error. Data in this table are also presented in units of kg/hectare-year (based on total compound molecular weight and not only carbon) for comparative purposes. Confidence limits (95%) were calculated as twice the standard error. In all cases, zero (no flux) was within the 95% confidence limits for measured values. Predicted and measured flux rates varied considerably, but were always within a factor of 10. For site FB, predicted flux rates for the aromatic species--benzene, indene and styrene--were all approximately 3.5 times higher than measured rates. The predicted flux rate for the aromatic class was 4.8 times higher than the measured rate. However, the predicted rate for diethyl ether was only 0.35 (35%) of the measured rate. Predicted flux rates for diethyl ether and styrene were within the 95% confidence limits for the measured rates, while benzene, styrene and the aromatic class fell outside the 95% confidence limits.

For site TB, predicted flux rates were greater than the measured rates for benzene and cyclohexane by factors of 10.0 and 5.9, respectively. These differences should be viewed in light of the low measured rates for these compounds, which were considerably lower than flux rates at site FB. The predicted flux rate for acetone was 0.15 (15%) of the measured rate at this site. The predicted flux rate for acetone fell within the 95% confidence limits for the measured value, while predicted flux rates for benzene and cyclohexane at this site did not.

In summary, predicted flux rates range from 0.15 to 10 times the measured flux rates at two sites. Predicted rates for aliphatic and aromatic hydrocarbons were always higher than measured rates, while predicted rates for the two polar species, diethyl ether and acetone, were lower than the measured rates. The lower predicted flux rates for the polar compounds can possibly be attributed to low analytical data on these compounds in water, since these do not purge efficiently using routine purge and trap techniques. Data from site FB should also be viewed in light of the fact that VOC species concentrations in the water (used for predictive modeling) were not obtained on the same day as air flux rate data were obtained.

The predictive modeling demonstrated relative contributions of the turbulent and convective mass transfer coefficients to the overall mass transfer coefficients for the two sites. These data are presented in Table 7-15. Only site FB contained aerators which provide turbulent phase mass transfer. Data presented in Table 7-15 demonstrate that for the aerated pond the turbulent phase mass transfer contributed up to 85-95% of the overall emissions.

TABLE 7-14. COMPARISON OF PREDICTED AND MEASURED FLUX RATES

Species or Class	Predicted Flux		Average Measured Flux[a]		Predicted	Measured Flux Confidence Limits (95%)[b]		Predictive Flux Within Limits?
	ng-C/cm^2-sec	kg/hectare-yr	ng-C/cm^2-sec	kg/hectare-yr	Measured	ng-C/cm^2-sec	kg/hectare-yr	
Site = FB								
Benzene	0.208	7,150	0.0592 ± 0.0492	2030 ± 1680	3.5	0 - 0.158	0 - 5390	No
Diethyl Ether	0.0266	1,300	0.0751 ± 0.0561	3660 ± 2730	0.35	0 - 0.187	0 - 9120	Yes
Indene	0.0889	3,010	0.0261 ± 0.0167	880 ± 570	3.4	0 - 0.0595	0 - 2020	No
Styrene	0.0438	1,500	0.0126 ± 0.0261	430 ± 890	3.5	0 - 0.0647	0 - 2210	Yes
Total Aromatics	0.586	20,400	0.120 ± 0.0829	4180 ± 2890	4.8	0 - 0.286	0 - 9960	No
Site = TB								
Benzene	0.0394	1,340	0.0038 ± 0.0138	130 ± 480	10.0	0 - 0.0313	0 - 1090	No
Cyclohexane	0.0381	1,400	0.0065 ± 0.0134	230 ± 490	5.9	0 - 0.0333	0 - 1210	No
Acetone	0.00458	240	0.0313 ± 0.0168	1550 ± 860	0.15	0 - 0.0650	0 - 3270	Yes

[a] Mean ± standard error (σ)

[b] Mean ± 2σ

TABLE 7-15. RELATIVE CONTRIBUTIONS OF TURBULENT AND CONVECTIVE REGIONS TO MASS TRANSFER COEFFICIENTS

Species or Class	K_L [a] (lb-mole/ft^2-hr)	$(K_L)_C$ [b] (lb-mole/ft^2-hr)	Convective Contribution [d] to K_L (%)	$(K_L)_T$ [c] (lb-mole/ft^2-hr)	Turbulent [e] Contribution to K_L (%)
Site = FB					
Benzene	0.038	0.025	63.0	0.455	35.9
Diethyl Ether	0.143	0.088	59.7	1.91	40.1
Indene	0.00093	0.0007	73.0	0.0082	26.5
Styrene	0.0021	0.0015	69.3	0.021	30.0
Total Aromatics	0.0033	0.0024	70.5	0.031	28.2
Site = TB					
Benzene	0.041	0.041	100	--	--
Cyclohexane	0.036	0.036	100	--	--
Acetone	0.092	0.092	100	--	--

[a] K_L - Overall mass transfer coefficient.

[b] $(K_L)_C$ - Convective liquid phase mass transfer coefficient.

[c] $(K_L)_T$ - Turbulent phase mass transfer coefficient.

[d] $A_C/A = 0.97$.

[e] $A_T/A = 0.03$.

SECTION 8

QUALITY ASSURANCE/QUALITY CONTROL RESULTS

The work performed during this program incorporated a comprehensive quality assurance/quality control (QA/QC) program as an integral part of the overall sampling and analytical effort. The primary objective of the QA/QC program was to provide a system for defining the measurement data quality in terms of precision and accuracy. It also provided a mechanism for assuring that the data were representative, complete, and comparable to other similar data.

The quality assurance function was organized to provide an independent review and assessment of project activities and their ability to achieve the stated data quality objectives. The QA coordinator for the project had the responsibility for evaluating the adequacy and effectiveness of the QC system and providing assurance that it was, in fact, responsive to the specific needs of the program.

While the system of QA activities was necessarily independent of the technical effort per se, the QC system was an integral part of the daily technical effort. It was designed to provide an overall system for generating data of a specified quality.

This section addresses both QA and QC activities and results. The QA efforts discussed here were primarily related to performance and systems audits which were conducted during the program. The internal QC system is also discussed and results are presented for the QC analyses.

QA/QC SUMMARY

The data capture for this project is presented in Table 8-1. The measurements used in defining data capture are only those which were required for input to the flux or predictive model calculations. The total number of data measurements are presented in Table 5-1. A large number of data points were collected for meteorological data. However, these were averaged to provide one temperature and one wind speed measurement at each of the six heights for six test runs. The maximum number of air temperature measurements then was six heights for six sets, or 36. If one of the six parameter measurements was discarded statistically, then it was not included in data capture. The number of air temperature and wind speed measurements used in the flux calculations is discussed in Section 7. Of the 36 scheduled air samples, 35 were collected and analyzed. Although 80% VOC species identification was not achieved on all air samples, all species which demonstrated concentration variations with height were identified. All water samples were collected.

TABLE 8-1. DATA CAPTURE FOR VOC POND SAMPLING AND ANALYSES*

MEASUREMENT PARAMETERS	SCHEDULED MEASUREMENTS	MEASUREMENTS PERFORMED WITHIN QC LIMITS	DATA CAPTURE
Air Temperature	6 X 6 = 36	30	83%
Wind Speed	6 X 6 = 36	33	92%
Humidity	1 x 6 = 6	6	100%
Water Temperature	1 x 6 = 6	6	100%
Air Samples	6 x 6 = 36	35	97%
Water Samples	1 x 6 = 6	2	33%
TOTAL*	126	112	89%

*Includes only those measurements required for flux or predictive model calculations. All replicate measurements were reduced to the number of data points required for these calculations. For the acutal number of measurements, see Table 5-1.

However, most of the water samples were lost during storage due to equipment malfunction and, therefore, data are not available for these. The overall data capture for all measurements directly relating to flux and predictive model calculations was 89%.

A summary of estimated and actual precision, accuracy and data capture is presented in Table 8-2. The overall precision listed for C_2 - C_{10} VOC species considers sampling and analytical variabilities. Measured precision values for VOC species are greater than estimated values because the species measured were at very low concentrations. Results presented in the section, Nested Sample Results: Ambient Data Precision, show that sampling and analytical variances accounted for 9% to 78% of total variances in species concentrations measured at the different sampling heights. The precision listed for wind speed measurements was not measured directly, but instead, was obtained from audit results. Precision of temperature measurements was within the expected value. Precision data will be discussed in the following sections. Measured accuracy values for VOC species and wind speed measurements were well within the estimated limits. The measured accuracy for temperature measurements was slightly higher than the estimated value. Accuracy data were obtained from independent audits and are discussed in the section, Performance and System Audits. Data capture for VOC species and wind speed were within the estimated limits. However, data capture for temperature measurements were below the estimated limit.

METHODS OF QUANTITATING DATA QUALITY

The performance audits and QC analyses conducted during the VOC pond emissions program were designed to provide a quantitative assessment of the measurement system data. The two aspects of data quality which are of primary concern are precision and accuracy. Accuracy reflects the degree to which the measured value represents the actual or "true" value for a given parameter, and includes elements of both bias and precision. Precision is a measure of the variability associated with the measurement system.

The data necessary for assessment of precision and accuracy were obtained in several ways. The performance audits for ambient air sampling and analysis were meant to measure accuracy of the measurement systems and consisted of submitting audit samples for analysis by the various methods used for field sample analyses. In the case of real-time monitoring instrumentation (e.g., temperature and wind speed), special instrumentation designed to measure the system accuracy was used. Variability (precision) associated with the various components of the ambient air sampling and analytical systems was measured and documented using QC procedures such as control sample analyses, instrument linearity checks and nested samples. These procedures are discussed in more detail in the following sections.

While the performance audits were primarily meant to measure accuracy of the measurement sytsems, in the case of VOC data, the results provided some insight into the precision as well as the bias of measurements. These precision data supplement data generated by the internal QC procedures. Extrapolation of the audit and QC data to actual samples and measurements provided the primary mechanism whereby error limits for the various

TABLE 8-2. SUMMARY OF ESTIMATED AND ACTUAL PRECISION, ACCURACY AND DATA CAPTURE

MEASUREMENT PARAMETERS	PRECISION		ACCURACY[a]		DATA CAPTURE[b]	
	Estimated	Measured	Estimated	Measured	Estimated	Actual
C_2 - C_{10} VOC Species	25%	34%[c]	±35%	-12%	80%	97%
Wind Speed	1%	1.8%[d]	± 5%	-0.2%	≥90%	92%
Temperature	1%	0.9%[e]	±2%[d] (±0.5°C)	2.6% (0.7°C)	≥90%	83%

[a] Overall mean relative error based on performance audit results
[b] Valid data percentage of total tests scheduled
[c] Pooled coefficient of variation
[d] Pooled standard deviation of the relative error measured during performance audit
[e] At 25°C

various measurements were estimated and the confidence in the measurement data defined.

The audit data are summarized in terms of "relative error", or "%Δ". This reflects the degree to which the measured value agrees with the actual value, in terms of percent of the actual value:

$$\text{Relative error } (\%\Delta) = \frac{\text{Measured value} - \text{Actual value}}{\text{Actual value}} \times 100\%$$

This way of expressing accuracy allowed for a comparison of accuracy at different levels (e.g., different concentrations), and for different parameters of the same type (e.g., different compounds analyzed by the same method). In summarizing the audit results, mean relative errors are presented in each table. In most cases, the variability in these error measurements reflected one aspect of the overall precision associated with the measurement system. This variability was quantitated in terms of the standard deviation of the mean relative error, which is also presented.

A second way of estimating variability, or precision of the measurements, is to determine the variability of replicate analyses and replicate samples. A convenient and accepted way of expressing this variability is in terms of the coefficient of variation (CV) for the replicates, where:

$$\text{CV} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

CV data for replicate samples and replicate analyses are presented for both QC analyses and audit samples. With respect to the audit data, this term is independent of the error (accuracy) of the analyses and reflects only the degree to which the measurements agree with one another, not the degree to which they agree with the "true" value for the parameter measured. The CV is in units of percent since it is the standard deviation of the mean expressed as percent of the mean (relative standard deviation).

In assessing the QC data and audit results, examples are helpful. For the nine-component audit samples, an overall mean relative error of -10.3% is reported. The pooled standard deviation (i.e., "average" standard deviation) of these data is 23.7% and values of 15.4% and 2.8% are reported for the CV for the duplicate analyses. The overall mean relative error is a measure of the bias of the analytical data. The significance of this mean can be assessed using confidence intervals. An approximate 95% confidence interval for the mean relative error can be calculated using:

$$\text{Mean relative error } \pm t_{0.25,\,(n-1)} \left(\frac{\text{Standard Deviation}}{\sqrt{n}} \right)$$

where n is the number of results used to compute the average and standard deviation and t is a table statistical value (0.25 confidence level, n-1 degrees of freedom; when n is greater than 10, t approaches 2.0). For the nine-component audit sample, the 95% confidence interval is:

$$-10.3 \pm 2.1\left(\frac{23.7\%}{\sqrt{18}}\right)$$

$$\text{or } (-22\%, 1.4\%)$$

Since this confidence interval includes zero, a conclusion of bias is not justified.

The CV for replicate samples and/or replicate analyses is a measure of the variability associated with the analyses (or preparation, dilution, sampling, etc., as appropriate). Approximately 95% of the results can be expected to fall within ±2 CV about the average measurement.

Correlation analysis is another statistical technique used for data analysis during this program. The least squares method of linear regression analysis was used as a quality control procedure for the GC/FID/PID analyses. Linearity check standards (propane and hexane) were analyzed at three levels on a biweekly basis. These data, along with system blank data, were then evaluated using linear regression to define the linearity of the instrument response over the working range. A control limit of 0.99 was set for the correlation coefficient, r, calculated as:

$$r = \frac{n(\Sigma XY) - (\Sigma X)(\Sigma Y)}{\sqrt{n(\Sigma X^2) - (\Sigma X)^2}\sqrt{n(\Sigma Y^2) - (\Sigma Y)^2}}$$

where:

X = the amount of carbon in the standard (nL-C)

Y = the instrument response (peak area).

In addition to the linearity check, these data also provided reference response factor values (nL-C/unit area) for comparison to response factors for the daily quantitative standard. These QC procedures are detailed below.

When different variances were combined (pooled) to obtain an overall variance, such as combining species variations to obtain a chemical class variation, the following technique was used:

$$V = \left[\frac{n_a V_a{}^2 + n_b V_b{}^2 + n_c V_c{}^2 \cdots}{n_T}\right]^{1/2}$$

where:

V = pooled variance

$n_a, n_b, n_c \ldots$ = number of observations for variances a, b, c... etc.

$V_a, V_b, V_c \ldots$ = variances of measurement a, b, c... etc.

n_T = combined observations, $n_a + n_b + n_c + \ldots$ etc.

In assessing the data quality for any given measurement system, audit results should always be considered along with data quality measurements associated with the internal QC system for that measurement. This includes data for replicate samples, replicate analyses, control samples, nested samples, blanks, etc. The various internal QC and audit procedures are discussed and data associated with these procedures are presented in the following sections.

QUALITY CONTROL FOR ONSITE SAMPLING

Routine quality control for onsite sampling included those procedures relating to meteorological measurements and collection of air samples. In addition, quality control limits were specified for proper meteorological conditions prior to initiation of sampling. All of these are discussed in this section. Quality control procedures are discussed as calibrations performed prior to field sampling and results of routine procedures performed onsite. All quality control data for calibrations are presented in Appendix D. Quality control data for onsite procedures are also presented in Appendix D, unless these data directly affected data used for flux calculations.

Sampling System and Meteorological Instrumentation Calibration

Prior to field sampling, calibrations were performed on all temperature and wind speed measurement instrumentation, and the ambient air sampling system. The wind direction sensor was calibrated at the field sites. All raw calibration data were recorded on calibration forms, as specified in the Quality Assurance Project Plan (QAPP)(7). These are presented in Appendix D.

Temperature--

The temperature sensors were tested by placing the sensors in a temperature controlled bath. This test verified the sensor accuracy and the results obtained from the normal data recording system. All temperatures in the bath were verified against an NBS traceable thermometer. The accuracy of the temperature translators was checked with a calibrated decade resistance source. Resistances which corresponded to precise temperatures were input to the translator. Responses were taken from the data system and verified with a digital voltage meter for accuracy.

Humidity--

It was stated in the QAPP that the humidity sensor would be calibrated against a Psychro-Dyne psychrometer. The humidity probe was not used due to inaccuracies. Instead, the psychrometer was used for all measurements. No quality control was performed on this instrument, but its operation was checked during the quality assurance audit.

Wind Speed--

Wind speed sensors were calibrated using synchronous motors to verify the accuracy of the transducers. Synchronous motor speeds corresponding to known wind speeds were used to actively check the wind speed system from sensor to data recording. In addition, linearity and accuracy were determined for each wind speed translator by using a frequency generator and counter. The frequencies input to each translator corresponded to known wind speeds. The results were checked on the data system and verified with a digital volt meter for accuracy. Five frequencies were input for each wind speed system.

Wind Direction--

Wind direction data were used to demonstrate the constancy of wind direction. The wind direction sensor was calibrated onsite by aligning the sensor benchmark to north with a compass after the boat position was established. This assignment was valid for only the position the boat was in at that time. The boat was routinely positioned directly into the wind. After the boat was anchored in a stationary position, the constancy of wind direction was monitored with this sensor.

Vacuum Flow Regulators--

Vacuum flow regulators were used to provide a constant sample flow rate over a given period of time and over a large pressure differential. These regulators were set and calibrated by connecting each in line with an evacuated canister and filter, and monitoring air flow at the filter inlet with a mass flow meter and strip chart recorder. Each vacuum flow regulator was set and marked to provide the appropriate flows for the 20-minute sampling period. In addition, a flow differential diagram was constructed for each regulator over the sampling period and for the required canister pressure differentials. For the sampling, it was not critical to know the exact flow produced by each flow regulator since this did not enter into data calculations. However, it was important to know the flow variation produced by each flow regulator over the sampling period. These data were provided in each flow differential diagram. Only regulators which produced a constant flow rate in the laboratory were used for field sampling. Flow differential diagrams for the regulators which were used are presented in Appendix D.

Onsite Quality Control

Onsite quality control involved the following routine checks of correct instrument response. These were performed once at each sampling site.

Wind Speed--

Wind speed sensors were zeroed each day by removing all cups and operating the sensors for a 20-minute period. An example of the wind speed sensor check for site TB is presented in Table 8-3. No corrections to the measurements collected for wind speed were required.

Temperature--

Temperature sensors and translators were checked at each site by operating all sensors at the same height for a 20-minute period. The temperature sensor check for site TB is presented in Table 8-3. Since

TABLE 8-3. QUALITY CONTROL CHECKS - EXAMPLE WIND AND TEMPERATURE SENSOR DATA REPORT

STATION 001 1240 03/18/82

TIME	WDRT DEG	WS1 MPH	WS2 MPH	WS3 MPH	WS4 MPH	WS5 MPH	WSR MPH	WSA TMPH	WDA DEG	TMP1 DEGF	TMP2 DEGF	TMP3 DEGF	TMP4 DEGF	TMP5 DEGF	TMP6 DEGF	WDAV DEG	WGUST MPH
1220	90	0	0	0	0	0	0	0	84	81	82	82	84	82	81	11	0
1222	90	0	0	0	0	0	0	0	84	81	81	82	84	82	81	20	0
1224	90	0	0	0	0	0	0	0	85	80	80	80	83	80	81	24	0
1226	90	0	0	0	0	0	0	0	82	81	81	81	83	81	81	4	0
1228	90	0	0	0	0	0	0	0	82	81	82	82	83	82	80	3	0
1230	90	0	0	0	0	0	0	0	82	81	82	82	83	83	80	3	0
1232	90	0	0	0	0	0	0	0	82	81	82	82	83	83	80	3	0
1234	90	0	0	0	0	0	0	0	82	82	82	82	84	82	82	3	0
1236	90	0	0	0	0	0	0	0	83	82	82	82	84	83	82	4	0
1238	90	0	0	0	0	0	0	0	83	82	82	82	84	83	82	4	0
AVG	0	0	0	0	0	0	0	0	83	81	82	82	84	82	81	9	0

*All wind and temperature sensors operated at same height the measured temperature was not the same for all sensors, correction factors were calculated and applied to collected data. The correction factors for temperature measurements are presented in Table 8-4.

TABLE 8-4. CORRECTION FACTORS FOR TEMPERATURE MEASUREMENTS (°F)

Probe No.	1	2	3	4	5	6
Offset Site FB	+0.4	0	-0.1	-1.9	-0.5	+0.6
Offset Site TB	+1.0	0	+1.0	0	-1.0	-2.0
Correction Factor	+0.7	0	+0.5	-1.0	-0.8	-0.7

Data presented in Table 8-3 were used to calculate precision for temperature measurements. Precision for the six temperature probes ranged from 0.63% to 1.2%. The pooled precision for all six probes was 0.9%.

QC Meteorological Limits--

Data had to be collected during proper atmospheric conditions for use in the Concentration-Profile technique. The determination of atmospheric conditions was discussed in Section 3. If these conditions were not met, then sampling preparations were not initiated.

A summary of the meteorological conditions which were measured prior to sample collection is presented in Table 8-5. In all cases, all QC tests were passed prior to sample collection. The Richardson numbers (see Section 3) presented in this table confirmed the manual inspection of atmospheric stability class.

Sampling System Quality Control Samples--

A list of the quality control samples which were proposed and those which were collected in the field is presented in Table 8-6. Six sampling system blanks were collected, one at each sampling height. Three system blanks were collected at site FB (arms one, two and three) using Radian stainless steel canisters and three were collected at site TB (arms four, five and six) using EPA stainless steel canisters. The purpose of the blanks was to determine VOC species which were being introduced to the ambient mast data by the sampling system. Sampling system blanks were collected by connecting a tank of UHP air to the probe inlet filter and collecting a 20-minute integrated sample.

TABLE 8-5. SUMMARY OF QC LIMITS FOR PROPER METEOROLOGICAL CONDITIONS PRIOR TO SAMPLING

Meteorological Parameter	Quality Control Limit	Observed Value					
		Site FB			Site TB		
		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Manual estimation of atmos. stability class	D,E,F	D	D	D	D	D	D
Wind speed at Level 6	> 5 mph	10	11	11	17	19	22
Maximum 1 second wind gust (mph)	< 3 times ave. wind speed	18	15	16	25	30	31
Wind direction standard deviation	< 45°	25°	6°	6°	19°	18°	11°
Richardson number	> -0.1	-0.077	-0.059	-0.104	-0.024	-0.011	-0.017

TABLE 8-6. PROPOSED AND COLLECTED QUALITY CONTROL SAMPLES

Sample Type	# From Site TB	# From Site FB	Total	Total Collected
System Blanks	3	3	6	6
Cartridge Samples	1	2	3	2
Cartridge Blanks	1	1	2	2
Duplicate Canister	2*	4	6	6
Total	7	10	17	16

* Duplicate sample collected, but not used as a nested sample since the EPA canister used could not be analyzed in duplicate.

Results of the sampling system blanks are presented in Table 8-7. Concentrations of the two major VOC species observed and the TNMHC are presented for each blank. The quality control limit for sampling system blanks was 100 ppbv-C TNMHC. All of the blank samples exceeded this level with the exception of two of the Radian canisters. The average blank level for the Radian canisters was 73 ppbv-C and the highest individual species concentration observed was 17.2 ppbv-C. The average blank level for the EPA canisters was 449 ppbv-C and the highest species level was 102.3 ppbv-C. A good deal of the contamination was from C_2 compounds (ethane, ethylene and acetylene). The contamination observed in the blanks was considered when selecting compounds for flux calculations.

Cartridge samples and blanks were collected for comparisons with results from canisters. It was learned during the field testing that the sorbent cartridges were not sealed properly. This is shown for the two cartridge blanks in Table 8-7. Data for the cartridge samples are presented in Appendix B (code numbers 027 and 026). These were collected simultaneously with canister samples 021 and 071, respectively (also in Appendix B). In general, the cartridge samples showed significantly higher levels of VOC species due to contamination resulting from improper sealing.

Duplicate samples were obtained by simultaneously collecting two canister samples, using two separate sampling probes, always at mast arm two. The duplicate canister samples from site FB were collected in Radian 2.8 L canisters. Each of the canisters was analyzed in duplicate. These results are presented below. The duplicate sample collected at site TB used one Radian canister and one EPA canister. Because of the small volume of the EPA canister (1 L), the sample could not be analyzed in duplicate for use in the nested sample analysis. A comparison of the results obtained using the Radian and EPA canisters for simultaneous duplicate sample collection is presented in Table 8-8. The compounds observed in both canisters were very

TABLE 8-7. MAJOR VOC SPECIES OBSERVED IN SAMPLING SYSTEM BLANKS AT EACH SITE

Sampling Arm	Site	Container[1] Type	Code #	TNMHC (ppbv-C)	Major Species I and Concentration (ppbv-C)		Major Species II and Concentration (ppbv-C)	
1	FB	Rad S.S.	033	51.2	Toluene	7.8	2,5-Dimethylhexane	7.2
2	FB	Rad S.S.	034	37.9	Benzene	8.4	Chloromethane	5.3
3	FB	Rad S.S.	035	129.4	n-Decane	17.2	Toluene	11.9
4	TB	EPA S.S.	050	689.0	Ethylbenzene	102.3	Total C_2	92.3
5	TB	EPA S.S.	051	111.6	Total C_2	43.5	Isobutene	9.7
6	TB	EPA S.S.	052	545.5	Total C_2	83.9	Cyclohexane	78.2
-	FB	Cartridge	086	907.4	Total C_2	538.5	Total C_3	46.0
-	TB	Cartridge	087	721.0	Total C_2	321.7	Unid. C_8 Alkane	91.9

[1] Rad S.S.= Radian stainless steel canister; EPA S.S.= EPA stainless steel canister; Cartridge = multisorbent cartridge

TABLE 8-8. COMPARISON OF RESULTS OBTAINED USING RADIAN S.S. AND EPA S.S. CANISTERS FOR SIMULTANEOUS DUPLICATE SAMPLE COLLECTION

Selected Compound or Class	Radian Canister #054 (ppbv-C)	EPA Canister #059 (ppbv-C)	Percent[1] Difference
Total C_2	52.8	88.6	+ 68
Total C_3	~ D_2	6.8	--
Isobutene + 1-Butene	7.6	9.0	+ 18
n-Butane	7.5	--	--
Acetone	5.6	31.2	+457
2-Methyl-2-butene	3.8	5.8	+ 53
Isobuteraldehyde	3.8	4.9	+ 29
Buteraldehyde	7.9	14.4	+ 82
3-Methylpentane	3.1	--	--
Benzene	11.6	13.9	+ 20
Cyclohexane	3.2	7.0	+119
2-Pentanone	--	6.2	--
2,3,4-Trimethylpentane	3.2	--	--
Toluene	6.4	9.9	+ 55
3-Methylheptane	4.0	--	--
o-Xylene	6.1	10.5	+ 72
1-Nonene	6.9	8.5	+ 23
n-Propylbenzene	3.2	5.8	+ 81
1,3,5-Trimethylbenzene	3.3	7.2	+118
o-Ethyltoluene	3.9	4.7	+ 21
n-Undecane	4.0	8.9	+123
Diethyl ether	6.1	12.7	+108
Methylbutanone	--	6.6	--
2-Methyl-3-pentanone	11.9	5.3	- 55
Methylstyrene	3.1	8.5	+174
Unid C_9 alkane	10.3	5.8	- 44
Unid C_{10} alkane	3.1	--	--
Total alkanes	91.2	117.1	+ 28
Total alkenes and alkynes	18.3	23.3	+ 27
Total aromatics	37.6	60.5	+ 61
Total oxygenated HC	35.3	81.3	+130
Total NMHC[2]	182.4	282.2	+ 55

[1] Percent difference = $\dfrac{\text{EPA(ppbv-C)} - \text{Radian (ppbv-C)}}{\text{Radian (ppbv-C)}} \times 100$

[2] Total NMHC = total nonmethane hydrocarbon content

--as applied to species concentrations = below detection limits (3 ppbv-C) similar; however, the concentrations observed in the EPA canisters were higher. This trend seemed to be emphasized for the oxygenated and aromatic compounds.

QUALITY CONTROL RESULTS FOR SAMPLE ANALYSES

Because of the complexity of the analytical system for determining C_2 - C_{10} VOC species in ambient air, a thorough quality assurance/quality control program was incorporated into the sample analysis routine. The purpose of this QA/QC program was to provide a continuous assessment of the quality of data which were being produced. A list of the quality control procedures and limits concerning sample analysis is presented in Table 8-9. The results for each of the QC procedures presented in Table 8-9, with the exception of duplicate analyses, are discussed below. Duplicate analyses are discussed in the section, Nested Sample Results: Ambient Data Precision.

Detector Linearity Checks

Detector linearity checks were performed twice during the project. They were accomplished by analyzing different volumes of a propane/n-hexane quantitative standard. Analyses were performed using three different volumes of the standard and a zero point. The data were statistically analyzed using a least squares linear regression program. The quantity of carbon analyzed (nL-C) was the dependent variable and the integrated area the independent variable. Propane was used to check linearity for C_2 - C_4 species and n-hexane was used for C_5 - C_{10} species. A correlation coefficient was calculated for each set of data and used as a quality control check. The QC limit for the correlation coefficient was 0.995. Data for the FID linearity checks are presented in Table 8-10. During the course of this study, electronic difficulties with the Vista 401 CDS integrator were encountered, and a second integrator was required. One of the linearity tests was run on this integrator. All correlation coefficients were 0.9989 or greater for four linearity checks using two different compounds.

Propane/Hexane Single Point Calibrations

The FID was calibrated on a daily basis using a propane/hexane quantitative standard. As a quality control check of the detector response and stability, daily response was checked against the average response for the last linearity check. If the daily response for the detector deviated from the average linearity response by more than 20%, then corrective action was taken. The deviation was calculated as relative error using the Apple II data system. After each calibration, the daily response factors and linearity deviations for propane and n-hexane, and the PID/FID response ratio for n-hexane were printed out. Also, all calibration and relative error data were stored on disk to allow easy tracking of the FID response over a period of time.

The quality control chart for FID response factors is presented in Figure 8-1. Daily deviations for propane did not exceed the QC limit. For n-hexane, the QC limit was exceeded twice. The analytical system was checked on both of these occasions and no apparent problems were found.

TABLE 8-9. ROUTINE QUALITY CONTROL TESTS FOR SAMPLE ANALYSIS

Test	Number/ Frequency	Acceptance Criteria	How Treated
Detector linearity check	1/2 weeks	Correlation coefficient greater than 0.995	Tabular or control chart for correlation coefficient
Propane/hexane single-point calibration standard	1/day	± 20% of linear calibration response factor	Control chart for percent deviation
Multicomponent QC sample	1/day	± 30 percent quantitation and positive identification of 10 of 12 compounds	Control charts for each component and identification
Analytical system blank	1/week	< 20 ppbv-C	Tabular or control chart
Sample component identification	All samples	Quantitation and identification of 80% of carbon content	Tabular
Duplicate analyses	12	25% relative standard deviation between analyses	Tabular

TABLE 8-10. FID LINEARITY CHECKS FOR VOC SAMPLE ANALYSIS

Date	Parameter	Quantity nL-C	Area	Slope	Correlation Coefficient
3-16-82	Hexane[1]	0.0	0	378.9	0.9989
		107.0	34,829		
		213.9	79,020		
		320.9	120,347		
3-29-82	Hexane[2]	0.0	0	1,364.2	0.9999
		107.0	145,380		
		213.9	293,650		
		320.9	436,960		
3-16-82	Propane[1]	0.0	0	392.5	0.9999
		54.4	21,261		
		108.8	42,216		
		163.2	64,188		
3-29-82	Propane[2]	0.0	0	1,242.6	0.9990
		54.4	71,288		
		108.8	142,590		
		163.2	201,560		

[1] Vista 401 CDS Data System

[2] Hewlett-Packard 3390A Integrator

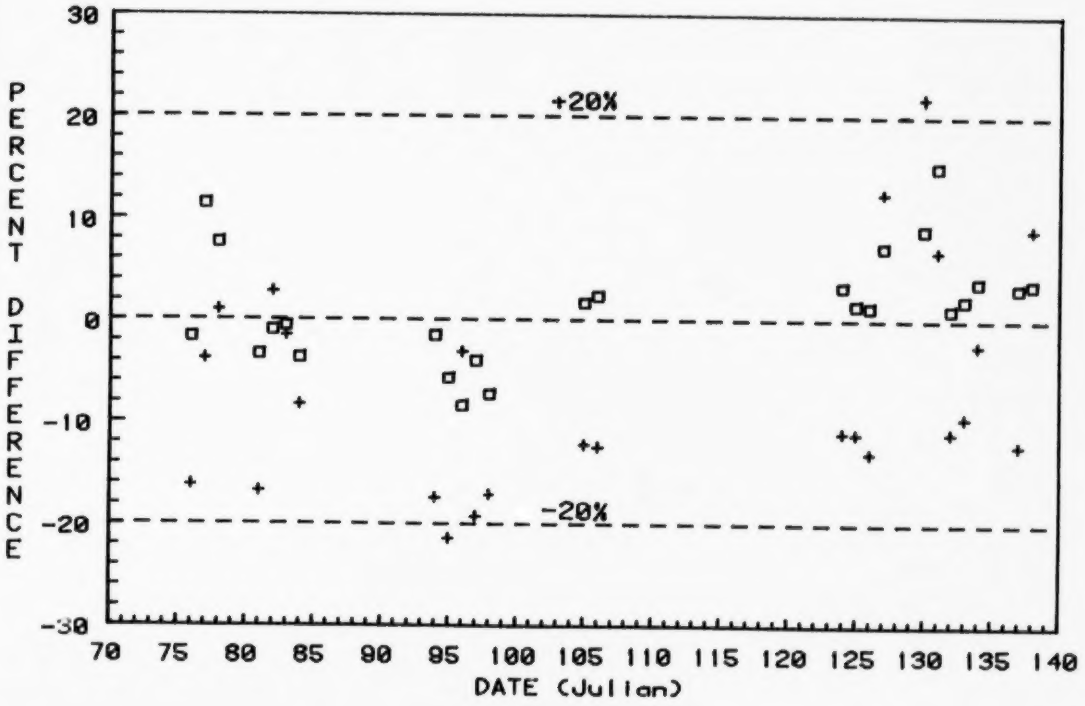

Figure 8-1. FID response factor control chart.

□ = Propane + = Hexane

Multicomponent QC Samples

A 12-component quality control standard was analyzed on all days when samples were analyzed. The purpose of this procedure was to demonstrate any deviations in the quantitative instrument response to various compounds and in qualitative identification of compounds by the computer auto-identification routines. The QC standard contained normal C_2 through C_{10} alkane species, isopentane, benzene, and toluene. Concentrations of the QC standard components varied from 23 ppbv-C for n-heptane to 414 ppbv-C for n-decane. All qualitative and quantitative data were taken from the Apple II output when it was operational. In some cases, a Hewlett-Packard integrator was used due to problems with the Vista/Apple system.

Quality control charts were maintained for quantitative evaluation of each component in the QC standard, and for qualitative identification of all components. An example QC chart for benzene is shown in Figure 8-2. Quality control charts for quantitative evaluations of each compound in the 12-compound mixture are presented in Appendix D. A ±30% QC limit was used on a daily basis to determine if corrective action was required. This limit was exceeded once for ethane and once for n-butane during the study.

Daily precision for all compounds in the QC standard are expressed numerically in Table 8-11. The worst cases were n-decane with a CV of 16% and n-nonane and toluene with CVs of 13%. The lower molecular weight components showed better precision. A CV of 3% was obtained for propane, and a CV of 8% was obtained for n-butane. The higher variation of ethane (12%) observed in this study is due to the peak sharpness of this species.

Component identification was performed using the Varian Vista 401 CDS and Apple II microcomputer data system. Identification schemes and windows are discussed in Section 4. The degree of positive identification for the 12-component QC standard is presented in Figure 8-3. The QC limit for automatic identification was a minimum of 10 compounds. This limit was not exceeded, and the minimum of 10 identifications was observed only twice. The missed identifications were not critical since all data were checked manually. The auto-identification scheme did not include information from the PID/FID TNR values.

Analytical System Blanks

Analytical system blanks were performed by analyzing approximately 1 L of UHP nitrogen. The procedure described for analytical system blanks in the Quality Assurance Project Plan (7) was to mimic the entire analytical procedure without trapping any gases. This procedure checked all portions of the analytical system for contamination except the moisture removal mechanism. It was learned that the Perma Pure driers were contributing some VOC species contamination to the samples. Since this contamination had to be quantitated and subtracted from sample data, the blank procedure was changed. The initial QC limit for analytical blanks was 20 ppbv-C. Results of analytical system blanks are presented in Table 8-12. With the exception of the 3/10/82 blank, all blank levels were higher than the initial QC limit,

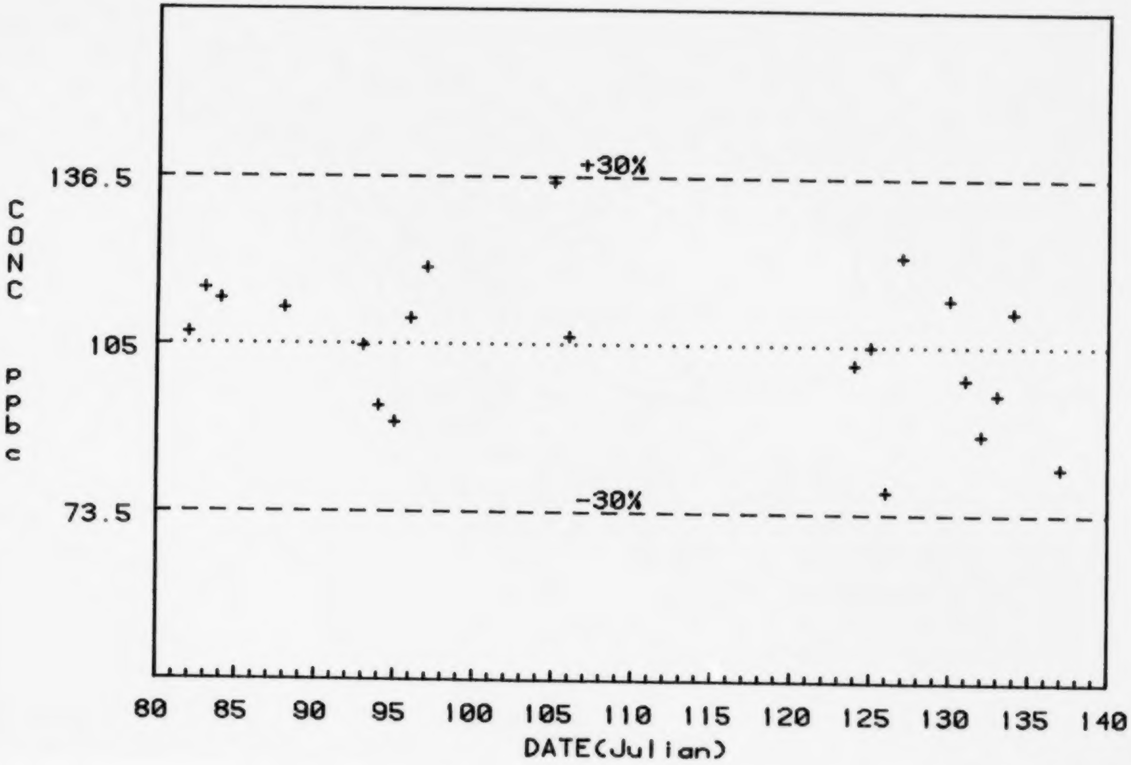

Figure 8-2. QC sample control chart for benzene.

TABLE 8-11. DAY-TO-DAY PRECISION ON THE 12-COMPONENT QUALITY CONTROL STANDARD

Component	Mean Concentration (ppbv-C)	Standard Deviation (ppbv-C)	Coefficient of Variation (%CV)
Ethane	43.4	5.34	12.3
Propane	115.4	4.00	3.5
Butane	57.9	5.66	9.8
Isopentane	24.6	2.43	9.9
Pentane	35.4	3.73	10.5
Hexane	63.0	6.64	10.5
Heptane	22.8	2.52	11.1
Octane	65.1	8.15	12.5
Nonane	167.9	22.95	13.7
Decane	414.5	67.92	16.4
Benzene	105.0	13.79	13.1
Toluene	241.1	29.32	12.2

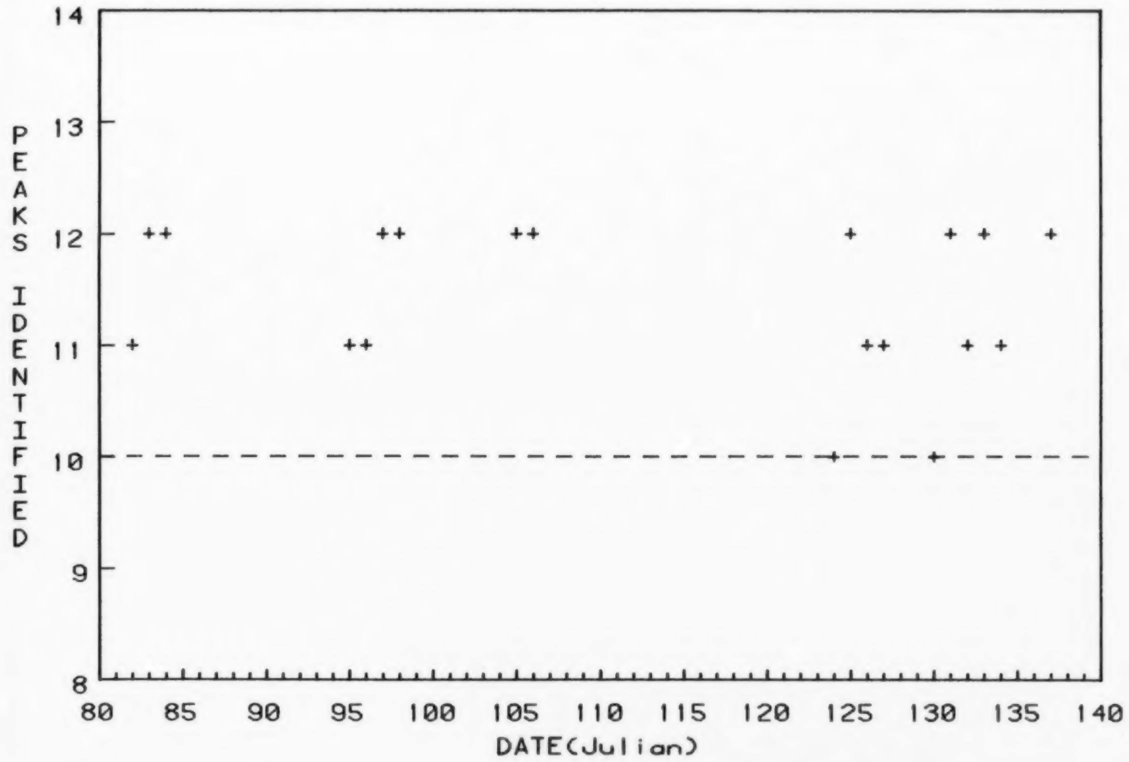

Figure 8-3. Positive identification of the 12-component QC standard.

mostly because of the addition of contaminants from the Perma Pure drier, and because UHP nitrogen contains approximately 20 ppbv-C.

TABLE 8-12. ANALYTICAL SYSTEM BLANKS FOR VOC POND PROJECT

Date	TNMHC (ppbv-C)
3/10/82	3.3
3/22/82	72.3
3/23/82	27.0
3/24/82	24.8
4/5/82	75.2
4/6/82	64.7
4/7/82	57.2
5/4/82	58.4
5/5/82	22.9
5/6/82	73.1
5/10/82	39.3
5/11/82	49.8

Analytical VOC blank levels were subtracted from the sample data. The analytical blanks varied somewhat with respect to the drier that was used. Three different driers were used during the course of the study. VOC contaminants produced by the Perma Pure driers were identified in the samples by means of relative retention times, and were subtracted from the sample data. In most cases, the blank levels did not correspond to known compounds in the peak table. However, a blank level of approximately 8 ppbv-C was obtained for benzene. This level was subtracted from benzene values observed in the samples.

Sample Component Identification

One of the analytical goals was to identify a minimum of 80% of the carbon content in each sample. A listing of the percentages of carbon identified for air and water samples is presented in Table 8-13.

For data presented in this table, only species identifications were considered. With the FID/PID technique, it was possible to classify all sample components into chemical classes with some degree of confidence. However, only chemical species can be immediately applied to the flux and predictive models. Greater than 80% species identification (QC limit) was obtained on 76% of the air samples and 29% of the water samples. This demonstrates that the samples encountered, especially the water samples, were significantly more complex than the ambient air samples for which the peak identification table was developed.

TABLE 8-13. PERCENTAGE OF HYDROCARBON IDENTIFICATION IN AIR AND WATER SAMPLES

Sample Type	Number of Samples	% VOC Identification				
		<60	60-70	70-80	80-90	90-100
Air	51	3	6	8	10	24
Water	14	3	4	3	4	0
Total	65	6	10	11	14	24

NESTED SAMPLE RESULTS: AMBIENT DATA PRECISION

Nested samples were collected and analyzed to help assess data variability introduced by the sampling and analytical procedures. The nested sampling and analysis procedure consisted of collecting simultaneous duplicate samples at the same height (arm 2) and analyzing each sample in duplicate. This resulted in four analyses for a single sampling height. The nested procedure allowed statistical evaluation of the data variability associated with sample collection and sample analysis. The nested procedure was performed twice, both times at site FB. Duplicate analyses could only be performed on the 2.8 L canisters. Due to a shortage of these, the duplicate canister sample collected at site TB used one 2.8 L canister and one 1.0 L canister.

Total Data Variability

Variability in the ambient data was due to sample collection, storage and analysis. The nested sampling procedure was designed to assess variability associated with each step of data acquisition. For this data treatment, species which were detected less than three times in a nested data set were separated from the main data. If a compound was detected only once during a duplicate analysis, the other value was input as one-half of the detection limit (1.5 ppbv-C). The total variability (expressed as CV, coefficient of variation) for each chemical species and the variabilities associated with analysis for each species are presented in Table 8-14. Two sets of nested samples were analyzed during the study. The number of nested samples that each species was observed in (three or more observations in each set) is presented in the second column of Table 8-14. The mean species concentration for the nested samples in which the species was observed is presented in the third column.

The total CV value presented in Table 8-14 includes variability due to all aspects of data acquisition: sample collection, storage, and analysis. These data are presented in column 4. Species variabilities due only to sample analysis are presented in the last column of Table 8-14. The total

TABLE 8-14. ANALYTICAL AND SAMPLING VARIABILITIES FOR HYDROCARBON SPECIES

Species	Nested Observations	Mean Concentration (ppbv-C)	Total CV Sampling & Analysis	CV Analysis
Total C_2	2	28.0	58.7	56.8
Total C_3	1	10.8	11.2	11.2
Isobutane	1	6.9	49.0	27.0
Acetaldehyde	1	3.4	78.5	24.8
n-Butane	1	6.0	19.6	18.3
t-2-Butene	1	9.6	27.1	8.8
c-2-Butene	1	3.4	13.3	9.8
Isopentane	1	4.3	33.8	26.8
Dichloromethane	1	7.4	37.0	7.0
Buteraldehyde	2	10.0	31.2	18.7
3-Methylpentane	1	12.0	29.8	15.9
Butanone	1	48.5	54.1	27.1
2-Methyl-1-pentene	2	8.0	28.9	17.1
Benzene	2	52.4	10.0	7.8
Valeraldehyde	1	9.8	45.0	6.2
3-Pentanone	1	12.9	67.7	67.7
Toluene	2	13.4	11.1	11.1
3-Methylheptane	1	8.7	8.6	8.6
m-Xylene	2	9.4	15.1	13.4
Styrene	2	14.2	14.5	7.3
n-Nonene	1	4.2	35.8	28.5
α-Pinene	1	5.0	13.7	13.7
n-Propylbenzene	1	9.3	3.9	2.7
n-Decane	2	8.3	42.2	29.1
n-Undecane	2	6.2	33.4	32.3
Diethyl ether	2	51.4	10.9	5.4
Methylbutanone	1	6.2	24.8	8.1
2-Methyl-3-pentanone	1	6.6	4.9	4.9
Indene	2	19.2	36.7	4.9
Methyl hexanone	2	13.0	35.8	24.4
Cyclopentanol	1	3.8	55.2	23.0
Total species	43	14.8	34.5	23.2

variability for all species was 34.5% with a mean species concentration of 14.8 ppbv-C. The analytical variability for all species was 23.2%. Analysis accounted for roughly 67% of the total sampling and analytical variability.

A compilation of variabilities for chemical classes is presented in Table 8-15. Variabilities in terms of CV for all species within chemical classes are presented along with variabilities for classes when summed for each sample. The total individual species variability (pooled CVs) as opposed to the TNMHC variability is also presented. As an example of interpreting these data, any species within the aromatic class may be expected to vary by 19%, while total aromatics may be expected to vary by 7%. Analytical variability for all species was 23%, whereas analytical variability for TNMHC obtained by summing all species within a sample was 8%. For most atmospheric photochemical dispersion models, the total class variability would be of primary importance.

The worst case analytical variability was 32% for alkane species. The worst case sampling and analytical variability was 43% for oxygenated hydrocarbon species. These data should be considered when examining species flux rates. To compare the importance of the variability factors presented in Table 8-15, Table 8-16 presents the hydrocarbon class variabilities along with the environmental variabilities. Environmental variabilities were calculated from average species or class concentrations for the two nested samples, and show how these may be expected to vary with respect to location on a given pond and time. For each class in Table 8-16, the mean concentration is presented, followed by components of variability for environment, sampling/storage, and analysis. The percent contribution of each component to the total variability is listed beneath each component of variability in parentheses. For example, one of the worst total (sampling and analytical) variabilities listed in Table 8-15 was for the oxygenated hydrocarbon class (28%). However, as observed in Table 8-16, this accounted for only 18.5% of the total environmental variability. The oxygenated hydrocarbon class also had one of the largest analytical variabilities (18%). This accounted for only 7.5% of the total environmental variability for oxygenated hydrocarbons. These data should be considered in light of the fact that the two sets of samples were collected at the same height on the same pond. Therefore, the environmental variability should be relatively small.

In Table 8-17, variance components for species used for flux calculations are presented. The variance components presented in the second column are for measurements of each species collected at six heights for the two runs in which nested samples were collected. Variabilities between the two runs were pooled, so that these data reflect only variability resulting from sample height, and not from position on the pond. In the third column, sampling and analytical variance components for each species are presented. The percentages of total height variability produced by sampling and analysis are presented in the final column of Table 8-17. These data demonstrate that for species such as benzene, diethyl ether, and the total aromatic class, variability due to sampling and analysis was negligible with respect to measured height variability. However, for higher molecular weight aromatic species such as styrene and indene, sampling and analysis were responsible for 25% and 78%, respectively, of measured total concentration variabilities.

TABLE 8-15. HYDROCARBON SPECIES CLASS AND TOTAL CLASS VARIABILITIES

Hydrocarbon Class	Nested Observations	Mean Response (ppbv-C)	Total CV Sampling & Analysis	CV Analysis
Alkane species	13	10.6	38.2	32.0
Total alkanes	2	69.5	24.3	23.9
Alkene species	5	6.8	23.5	13.8
Total alkenes	2	17.0	21.2	10.0
Aromatic species	11	19.5	19.1	9.0
Total aromatics	2	114.8	7.3	5.8
Oxygenated hydrocarbon species	13	18.8	43.1	24.7
Total oxygenated hydrocarbons	2	119.8	27.8	18.3
Chlorinated saturated hydrocarbon species	1	7.4	37.0	7.0
Total chlorinated saturated hydrocarbons	1	7.4	37.0	7.0
All species	43	14.8	34.5	23.2
TNMHC	2	325.4	11.6	7.8

TABLE 8-16. COMPONENTS OF VARIABILITY - CONTRIBUTIONS FROM ENVIRONMENTAL, SAMPLING AND ANALYTICAL SOURCES FOR HYDROCARBON CLASSES

Class	Mean Concentration (ppbv-C)	Environmental Variability Component* (% of Total)**	Sampling Variability Component* (% of Total)**	Analytical Variability Component* (% of Total)**	Analytical CV (%)
Alkanes	69.5	390 (57.7)	10 (1.5)	276 (40.8)	23.9
Alkenes and alkynes	17.0	124 (90.5)	10 (7.4)	3 (2.1)	10.0
Aromatics	114.8	47 (40.1)	26 (22.3)	44 (37.6)	5.8
Oxygenated hydrocarbons	119.8	5227 (82.5)	633 (10.0)	478 (7.5)	18.3
Chlorinated saturated hydrocarbons	7.4	0 (0.0)	7 (96.4)	0.3 (3.6)	7.0
TNMHC	325.4	8555 (85.8)	770 (7.7)	648 (6.5)	7.8

*Units of variance components are $(ppbv\text{-}C)^2$.

**Total is the sum of the three variance components.

TABLE 8-17. VARIABILITIES DUE TO SAMPLING HEIGHT FOR SELECTED COMPOUNDS

Species	Variance Component* Sampling Height + Sampling + Analysis	Variance Component* Sampling + Analysis	Sampling + Analysis % of Total
Benzene	223.0	27.4	12.3
Diethyl ether	333.5	31.2	9.4
Indene	63.4	49.4	77.9
Styrene	17.1	4.2	24.6
Total aromatics	1084.6	70.3	6.5

*Units of variance components are $(\text{ppbv-C})^2$

PERFORMANCE AND SYSTEM AUDITS

As part of the quality assurance effort for this project, both performance and systems QA audits were conducted. These audits addressed both field sampling activities and the off-site analysis of air samples. A systems audit of the sampling activities was conducted during sampling at site TB on March 19, 1982. The systems audit of the laboratory activities was conducted the following week. Systems audits were designed to provide an independent, qualitative assessment of the overall measurement effort and the associated internal QC system.

The performance audits for this project were designed to provide a quantitative assessment of the quality of measurement data. These audits were performed at several different times during the program. The methods used, results, and conclusions of both the performance and systems audits are presented in the following sections.

Performance Audits

In order to provide a basis for quantitative assessment of the accuracy of emissions measurement data, Radian QA personnel conducted performance audits of the two major measurement systems during the course of the project. The audit of the meteorological measurements system was performed during field sampling at site FB on March 16, 1982. The air sampling and analytical system audit consisted of submitting audit samples for analysis at several times during the project. One set of samples was submitted during the onsite audit at site TB on March 19, 1982. Table 8-18 summarizes the performance audit activities with respect to parameters/methods audited, audit standards used, and sources of the standards.

TABLE 8-18. SUMMARY OF PERFORMANCE AUDIT ACTIVITIES

Measurement Parameter	Method	Audit Standard(s)	Source of Audit Standards
VOC Emissions	GC/FID	Propane gas mixture. 12-component hydrocarbon mixture, and 9-component hydrocarbon mixture via dynamic dilution system.	Scott Environmental Technology, Inc.
Wind Speed	Anemometers	Frequency generator.	Radian (NBS traceable)
Temperature	Thermocouple	Decade resistance source.	Radian (NBS traceable)

Performance audits of the meteorological measurements system addressed the following instrumentation:

- six Weathertronics wind speed sensors,
- six Radian-built temperature sensors,
- a Weathertronics wind direction sensor, and
- a Psychro-Dyne relative humidity meter.

Each of the meteorological instruments was audited as an integrated system with the DART data acquisition system in accordance with calibration procedures outlined in the manufacturer's operations manual. The test equipment used for the audits was previously certified as NBS-traceable by an independent testing laboratory. The procedures used and audit results are presented below.

Wind Speed--

The cup anemometer wind speed sensors were audited using a calibrated frequency generator to input known frequencies to the wind speed translator. A Fluke Model 1900 frequency counter was used to verify the frequency input. The frequency inputs corresponded to specific wind speeds which, when compared to the system output, provided a measure of translator accuracy. Results for the wind speed audits are presented in Table 8-19. As indicated

TABLE 8-19. RESULTS OF PERFORMANCE AUDIT OF WIND SPEED SENSORS AT SIX LEVELS

Actual Value (mph)	Level 1		Level 2		Level 3		Level 4		Level 5		Level 6	
	Measured[a] Value (mph)	Relative[b] Error (%Δ)	Measured[a] Value (mph)	Relative[b] Error (%Δ)	Measured[a] Value (mph)	Relative[b] Error (%Δ)	Measured[a] Value (mph)	Relative[b] Error (%Δ)	Measured[a] Value (mph)	Relative[b] Error (%Δ)	Measured[a] Value (mph)	Relative[b] Error (%Δ)
0	-1	--	0	--	-1	--	1	--	1	--	0	--
25	24	- 4.0	24	- 4.0	25	0.0	26	4.0	24	- 4.0	25	0.0
50	50	0.0	50	0.0	49	- 2.0	50	0.0	50	0.0	50	0.0
75	75	0.0	75	0.0	75	0.0	75	0.0	76	1.3	75	0.0
100	100	0.0	101	1.0	100	0.0	100	0.0	101	1.0	101	1.0
Mean Relative Error[c]		- 1.0		- 0.8		- 0.5		1.0		- 0.4		0.3
Standard Deviation[d]		2.0		2.2		1.0		2.0		2.4		0.5

[a] Equivalent wind speed for standard frequency input.

[b] $\text{Relative error } (\%\Delta) = \frac{\text{Measured value - Actual value}}{\text{Actual Value}} \times 100$

[c] Mean relative error for nonzero measurements.

[d] Standard deviation of the relative error.

in the table, the wind speed sensors were quite accurate, with all six responding within ±1 mph for input values equivalent to a wind speed range of 0 mph to 100 mph.

Temperature--

Performance audits of the six temperature sensors were accomplished with an NBS-traceable decade resistance unit to input known resistances to the temperature sensor translators. Each resistance input was equivalent to a specific ambient temperature over the range of 0°F to 120°F. Comparison of the measured temperature to the equivalent temperature for each resistance input provided a measure of system accuracy. The results of temperature system audits are presented in Table 8-20. With the exception of the temperature sensor at level 1 (closest to water surface), all temperature translators responded to within ±2°F of input values. The level 1 translator responded to within ±5°F of audit inputs, and showed a significant zero offset of +7°F. In addition, a direct comparison audit of sensor response was performed by comparing the temperature measured by the level 1 and level 4 sensors to that measured using an NBS traceable mercury-in-glass thermometer. For an ambient temperature of 71°F, as measured using the reference thermometer, the level 1 sensor indicated a temperature of 72°F and the level 4 sensor indicated a temperature of 71°F.

Relative Humidity--

The Psychro-Dyne relative humidity meter used to measure ambient humidity was audited by comparison to an NBS-traceable aspirated psychrometer. This single-point audit indicated a relative error of -4.3% for the Psychro-Dyne instrument which indicated 91% humidity versus 95% based on the measurements using the reference psychrometer.

GC/FID/PID Analysis of Air Samples--

For the performance audit of off-site GC/FID/PID analysis of air samples, audit samples were submitted for analysis at several times during the project. Because these analyses were performed using an analytical technique which represents state-of-the-art technology, these audit results must be interpreted somewhat differently than the meteorological audit results. In the case of the meteorological measurements, the field instrumentation performance may be compared to accepted reference standards (e.g., NBS-traceable instruments) and the accuracy of the measurements defined with respect to the reference standards. However, there are no accepted reference standards for the air samples (e.g., standard gas mixtures). Gas mixtures may be obtained which contain representative hydrocarbon species, and are classified as "certified" standards. However, there are two major problems with accepting these standards as representing a "higher authority" in the sense of a true reference standard as typically used for audit purposes. First, there is difficulty in obtaining such mixtures at ambient (i.e., part per billion) concentrations. Second, the analytical technique used for certification of the standard cannot be considered to be inherently more accurate than that used for the sample analyses, and is possibly less accurate.

TABLE 8-20. RESULTS OF PERFORMANCE AUDIT OF TEMPERATURE SENORS AT SIX LEVELS

Actual Value (°F)	Level 1		Level 2		Level 3		Level 4		Level 5		Level 6	
	Measured[a] Value (°F)	Relative[b] Error (%Δ)	Measured[a] Value (°F)	Relative[b] Error (%Δ)	Measured[a] Value (°F)	Relative[b] Error (%Δ)	Measured[a] Value (°F)	Relative[b] Error (%Δ)	Measured[a] Value (°F)	Relative[b] Error (%Δ)	Measured[a] Value (°F)	Relative[b] Error (%Δ)
0	7	--	0	--	0	--	0	--	0	--	2	--
30	35	17.	31	3.3	31	3.3	32	6.7	31	3.3	32	6.7
60	63	5.0	61	1.7	60	0.0	61	1.7	61	1.7	61	1.7
90	91	1.1	91	1.1	91	1.1	91	1.1	92	2.2	91	1.1
120	119	- 0.8	121	0.8	121	0.8	121	0.8	121	0.8	121	0.8
Mean Relative Error[c]		5.5		1.7		1.3		2.6		2.0		2.6
Standard Deviation[d]		8.0		1.1		1.4		2.8		1.0		2.8

[a] Equivalent temperature for standard resistance input.

[b] Relative error (%Δ) = $\frac{\text{Measured value - Actual value}}{\text{Actual value}} \times 100$

[c] Mean relative error for nonzero measurements.

[d] Standard deviation of the relative error.

Because of the difficulty in obtaining stable hydrocarbon mixtures at ambient concentration levels, audit standards at these levels were prepared by dynamic dilution of part per million level mixtures. This was done using two capillary dilution systems. These systems used precision pressure gauges and calibrated capillary restrictors to measure and control the flows of UHP dilution air and the standard gas mixture. These were mixed in an inert, two-stage, flow-through mixing chamber. The capillary system and mixing chambers of the dilution system were contained in a heated enclosure to prevent adsorption of the gas components.

Several gas mixtures, containing different compounds and diluted to several different concentration levels, were used to assess the GC/FID/PID cryogenic focusing analytical technique. Although this may not be construed as an audit in the strictest sense, it does provide a means of comparative evaluation. While the precision and accuracy values inferred by the audit data are not judged to be absolutes, taken as a whole they are useful for defining the probable range of error associated with analytical data.

The results for the first set of audit samples are presented in Table 8-21. These samples were prepared during the field audit by dilution of a mixture of 197 ppm propane, 493 ppm methane, 493 ppm carbon monoxide and 9.97% carbon dioxide in air. The samples were collected in evacuated canisters using a 20-minute collection period, as was used for ambient sampling. As indicated in the table, there is good agreement for each pair of duplicate samples. The mean relative error was -22%. This included errors from initial dilution of the standard. In addition, the resulting gas was still at a higher concentration level than the working range of the analytical method.

The results for the second set of audit samples are presented in Table 8-22. Although these two samples were not prepared in duplicate, both samples were analyzed in duplicate. These samples were prepared by dilution of a nine-component mixture obtained from Scott Environmental Technology. The "actual" concentrations shown in this table were calculated based on the capillary dilution factor and analytical results reported by the Gas Kinetics and Photochemistry Branch (GKPB), U.S. EPA IERL-RTP. Generally, the agreement between the duplicates was quite good. Coefficients of variation for nine components at two concentrations ranged from 0.9% to 25.6% and the pooled CVs for each sample were 15.4% and 2.8%. Relative errors ranged from -73.5% to 94.2% with an overall mean of -10.3%. Results for the high molecular weight compounds in this mixture (n-propylbenzene and o-xylene) should be interpreted with caution. Although the dilution system used to prepare these samples was heat-traced, relatively low results for these compounds are possibly due to adsorption losses in the dilution system rather than sampling or analytical error.

The third set of audit samples included both duplicate samples and duplicate analyses. Two pairs of duplicate samples were prepared using a 12-component hydrocarbon mixture obtained from Scott Environmental Technology. One pair of duplicates was prepared by introducing the gas mixture directly into canisters without dilution. These two samples were subsequently analyzed in duplicate. The results of these analyses are

Table 8-21. RESULTS OF GC/FID/PID PERFORMANCE AUDIT FOR A PROPANE STANDARD PREPARED AT SITE TB

Sample #	Measured Conc. (ppmv-C)[a]	CV[b]	Actual Conc.	Relative Error[c] (% Δ)
082	0.470		0.552	-14.9
083	0.440	4.7	0.552	-20.3
084	1.45		1.77	-18.1
085	1.50	2.4	1.77	-35.0
	Pooled CV	3.7	Mean Relative Error	-22.1
			Standard Deviation	8.9

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[a] Parts per million by volume as carbon.

[b] Coefficient of variation for the duplicate samples, where

$$CV= \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

[c] Relative error = $\frac{\text{Measured Conc. - Actual Conc.}}{\text{Actual Conc.}} \times 100$

TABLE 8-22. RESULTS OF GC/FID/PID PERFORMANCE AUDIT FOR HYDROCARBONS (COMPONENTS AT TWO CONCENTRATIONS) CONDUCTED THE WEEK OF APRIL 7, 1982

	Sample # 089				Sample # 090					
	Mean Measured Conc. (ppbv-C)[a]	CV[b]	Actual Conc. (ppbv-C)[a]	Relative Error[c] (%Δ)	Mean Measured Conc. (ppbv-C)[a]	CV[b]	Actual Conc. (ppbv-C)[a]	Relative Error[c] (%Δ)	Mean Relative Error[d]	Standard Deviation[e] (n = 4)
Ethane	10.0	25.4	5.15	94.2	14.8	2.4	15.2	- 2.96	45.6	62.9
Propane	7.55	0.9	7.12	6.04	19.4	1.1	21.2	- 8.73	- 1.34	8.56
1-Butene + Isobutene	15.1	7.5	17.8	- 15.2	49.8	1.7	53.2	- 6.39	- 10.8	6.34
Cyclopentene	24.4	9.3	30.8	- 20.7	87.2	1.4	92.1	- 5.37	- 13.0	9.89
n-Hexane	28.9	7.3	37.9	- 23.7	104	1.7	113	- 7.96	- 15.8	9.73
Benzene	30.5	17.1	27.8	9.71	85.6	6.2	83.1	3.06	6.38	12.1
2,2,4-Trimethylpentane	48.5	4.7	65.5	- 26.0	181	2.1	196	- 7.52	- 16.8	10.9
n-Propylbenzene	23.4	25.6	88.5	- 73.5	152	2.7	264	- 42.3	- 57.9	18.4
o-Xylene	14.2	17.9	27.9	- 49.1	60.0	2.4	83.4	- 28.0	- 38.6	13.3
OVERALL[f]		15.4				2.8			- 10.3	23.7

[a] Parts per billion by volume as carbon.

[b] Coefficient of variation for the duplicate analyses by compound, where $\text{CV} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

[c] Relative error $= \frac{\text{Measured Conc. - Actual Conc.}}{\text{Actual Conc.}} \times 100$

[d] Mean relative error (%Δ) for the two samples, by compound.

[e] Standard deviation of the relative error, by compound.

[f] Overall pooled CVs, mean relative error, and pooled standard deviation for both samples, all compounds.

presented in Table 8-23. The other pair of duplicate samples were prepared by dilution of the same mixture. These results are presented in Table 8-24. The "actual" concentrations shown in these tables were calculated based on the "certified" concentrations reported by Scott Environmental.

Pooled analytical variabilities for the four samples (48 species measurements in duplicate) ranged from 9.5% to 15.7%. The mean relative error for the high concentration samples was -11.2% and for the low concentration samples -8.7%. Low results for n-nonane and n-decane in the low concentration samples could be attributable to the dilution system.

Correct species identifications were obtained for all species in all audit samples. A total of 122 species identifications were performed correctly in 8 samples (plus duplicate analyses). This figure is for 17 different species in the C_2 - C_{10} range. Two species were detected at low levels in samples H134 and H126 which were not listed in the standards.

In evaluating the data for all audit samples, it is important to consider several factors which influence the measurements. The first of these is concentration. Very high concentration samples such as those in Table 8-3 required serial dilution prior to analysis since the instrument was calibrated for samples at very low concentrations. The error which could be introduced in this step is roughly proportional to the degree of dilution required. As indicated in Table 8-24, the dynamic dilution technique used to prepare samples H133 and H134 is not without certain drawbacks. The relatively large errors for octane, nonane and decane in the samples is likely due to losses during dilution rather than analytical error.

Systems Audits

A systems audit is an on-site qualitative review of various aspects of a total sampling and/or analytical system to assess its overall effectiveness. It represents a subjective evaluation of a set of interactive systems with respect to strengths, weaknesses, and potential problem areas. The audit provides an evaluation of the adequacy of the overall measurement system(s) to provide data of known quality which are sufficient, in terms of quantity and quality, to meet the program objectives.

Systems audits of the various measurement systems used in the VOC pond emissions program were conducted at the time of the onsite audit and during the offsite analytical effort. Prior to the field audit, a checklist was prepared which delineated the critical aspects of the various methodologies using the work plan and Quality Assurance Project Plan (7) as guides. The checklist served as a tool to direct the focus of the systems audits and to document relevant observations. A copy of this checklist is presented in Appendix D. The systems audits conducted for this program consisted of observing and documenting activities associated with the various measurement systems (sampling, monitoring, and analytical) employed in the emissions characterization efforts. The audits were designed to evaluate the following:

TABLE 8-23. RESULTS OF GC/FID/PID PERFORMANCE AUDIT FOR HYDROCARBONS (12 COMPONENTS AT HIGH CONCENTRATION LEVELS) CONDUCTED THE WEEK OF MAY 2, 1982

Compound	Sample #H126				Sample #H127				
	Actual Conc.[a] (ppmv-C)	Mean Measured Conc.[b] (ppmv-C)[a]	CV[c]	Relative Error[d] (%)	Mean Measured Conc.[b] (ppmv-C)[a]	CV[c]	Relative Error[d] (%)	Mean Relative Error[e]	Standard Deviation[f] (n = 4)
Ethane	48.4	45.7	22.5	-5.6	33.5	42.9	-30.7	-18.2	25.6
Propane	50.4	53.7	1.6	6.5	51.5	4.2	2.2	4.4	3.7
n-Butane	44.4	49.4	0.7	-10.1	46.5	5.0	4.7	-2.7	4.8
Isopentane	49.2	58.7	3.4	19.1	55.5	3.1	12.8	16.0	5.7
n-Pentane	51.5	60.3	4.0	17.1	57.1	3.3	10.9	14.0	5.0
n-Hexane	48.2	55.4	6.6	14.9	52.9	4.7	9.8	12.4	6.1
Benzene	306	357	11.0	16.7	342	12.1	11.8	14.2	11.2
n-Heptane	51.7	56.5	10.3	9.3	54.9	10.8	6.2	7.8	9.4
Toluene	368	414	8.8	378	378	15.4	2.7	7.6	12.2
n-Octane	58.8	61.5	10.2	4.6	53.2	15.7	-9.5	-2.4	13.1
n-Nonane	53.6	61.1	7.6	14.0	46.3	13.3	-13.6	0.2	18.1
n-Decane	58.3	51.3	5.5	-12.0	36.5	10.4	-37.4	-24.7	15.4
Trichloroethylene		15.1		FP					
Overall[g]			9.5			15.7		-11.2	12.5

[a] Parts per million by volume as carbon.

[b] Mean value for duplicate analyses of each sample.

[c] Coefficient of variation for the duplicate analyses, by compound, where CV = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

[d] Relative Error (%) = $\frac{\text{Mean Measured conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

[e] Mean relative error for both samples (four analyses).

[f] Standard deviation of the relative error, by compound.

[g] Pooled coefficient of variation (CV), for each sample, overall mean relative error, and pooled standard deviation for all analyses.

FP = false positive, probable contaminant.

TABLE 8-24. RESULTS OF GC/FID/PID PERFORMANCE AUDIT FOR HYDROCARBONS (12 COMPONENTS AT LOW CONCENTRATION LEVELS) CONDUCTED THE WEEK OF MAY 2, 1982

		Sample # H133		Sample # H134				
Compound	Actual Conc.[a] (ppmv-C)	Measured Conc.[a] (ppmv-C)	Relative Error[b] (%)	Measured Conc.[a] (ppmv-C)	Relative Error[b] (%)	Mean Relative Error[c]	Standard Deviation[d] (n = 2)	CV[e]
Ethane	0.483	0.273	-43.4[f]	0.470	-2.7	-23.1[f]	28.8[f]	37.5
Propane	0.503	0.476	- 5.4	0.470	-6.6	- 6.0	0.84	0.9
n-Butane	0.443	0.442	- 0.2	0.423	-4.5	- 2.4	3.0	3.1
Isopentane	0.491	0.526	7.1	0.490	-0.2	3.4	5.2	5.0
n-Pentane	0.514	0.536	4.2	0.499	-2.9	0.6	5.0	5.0
n-Hexane	0.481	0.482	0.2	0.446	-7.3	- 3.6	5.3	5.5
Benzene	3.05	3.02	- 1.0	2.85	-6.6	- 3.8	4.0	4.1
n-Heptane	0.516	0.478	- 7.4	0.476	-7.8	- 7.6	0.28	0.3
Toluene	3.67	3.58	- 2.5	3.64	-0.8	- 1.6	1.2	1.2
n-Octane	0.587	0.505	-14.0[g]	0.527	-10.2[g]	-12.1[g]	2.7	1.4
n-Nonane	0.534	0.438	-18.0[g]	0.454	-15.0[g]	-16.5[g]	2.1	2.5
n-Decane	0.582	0.310	-46.7[g]	0.320	-45.0[g]	-45.8[g]	1.2	1.4
3-Methyl hexane		0.084	FP	0.074				
Overall[h]						- 8.7	9.1	11.2
C_3-C_8[i]						- 2.7	3.3	3.3

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[a] Parts per million by volume as carbon.

[b] Relative error = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

[c] Mean relative error (%) for the two samples by compound.

[d] Standard deviation of the relative error by compound.

[e] Coefficient of variation for the duplicate samples, by compound where CV = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

[f] Considered an outlier, not included in calculation of overall mean (%) and pooled standard deviation.

[g] Large errors for C_8-C_{10} compounds probably due to losses in dilution system and are not considered to reflect analytical error.

[h] Overall mean relative error pooled standard deviation and pooled CV for both samples, all compounds.

[i] Overall mean relative error pooled standard deviation and pooled CV for both samples, C_3-C_7compounds

FP = false positive, probably contaminant.

- sampling and analytical procedures,
- internal quality control procedures,
- chain-of-custody procedures,
- equipment and facilities,
- qualification and training of personnel,
- calibration documentation,
- sample handling and storage, and
- data recording validation.

As indicated on the audit checklist (Appendix D), careful compliance with the specified procedures was observed for both field testing/sample collection and analytical activities. The field crew and analytical personnel exhibited an obvious familiarity with the equipment and methods used. Internal QC procedures such as determination of atmospheric stability class prior to sampling, daily checks of the meteorological instrumentation, collection of blank and duplicate samples and analysis of control samples were carefully followed. The facilities and procedures used in sample handling, shipping and storage were considered to be adequate. All data records were well organized and the extensive use of computerized data acquisition and data reduction was judged to be a significant contribution to the overall data handling effort. The equipment calibration data were complete and similarly well organized. Overall, the systems audit indicated an efficient, well orchestrated sampling effort which was judged to be adequate for achieving the program requirements.

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The Appendices to this report have not been included because of their bulk. If the reader has need of this information, it can be obtained from the project officer: Paul de Percin at the address on the front of the report.